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THE SUSPENDING POWER OF DETERGENT SOLUTIONS

II. SOAP-BUILDER SOLUTIONS¹

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Abstract

Laboratory scale measurements have been made of the ability of certain alkaline salts, commonly used as laundry soap builders, to hold carbon particles in suspension, and thus prevent their deposition on fabric during the washing process. In the absence of soap little difference was noted between any of the builders studied, the suspending power being, on the whole, poorer than that of distilled water. In general, the addition of builders to soap solutions resulted in a decrease in the suspending power of the soap, this effect increasing with increasing builder concentration. The builders fall into three general classifications, viz.: simple electrolytes, silicates, and phosphates. Within each of these groups of builders the suspending power of a built soap solution increases with decreasing pH of the solution. A tentative explanation of the influence of added builders on the suspending power of soap solutions is offered, on the basis of interference with the normal adsorption of soap by the carbon particles, and, in some cases, the superimposed adsorption of the anion of the builder. Classification of the builders with respect to their effect on the suspending power of various pure soaps indicated that sodium hexametaphosphate is superior to all others, while sodium hydroxide and sodium orthosilicate are the poorest. There are only minor differences between the remaining builders, tetrasodium pyrophosphate and trisodium phosphate being the best in this group. This classification, which is based solely on suspending power, is not necessarily indicative of the over-all efficiency of builders in the detergent process as a whole.

In a previous paper (29) the importance of the soil redeposition factor in the detergent process was discussed, and data were presented relating to the suspending power* of solutions of pure soaps. In the present paper similar data are presented for solutions containing fixed amounts of pure soaps, together with varying amounts of certain alkaline salts which are commonly used as "builders" in commercial laundering practice.

Some work in this field has been reported previously, but measurements have been largely of the static type,* and have been carried out for the most part with noncarbonaceous soils (7, 10, 14, 20, 21, 26).

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* The term "suspending power" has been used in this and the preceding paper in accord with the definition given by Powney and Noad (17), i.e., to imply "the ability of a solution to prevent the adherence of solid particles to fibre surfaces under conditions of mechanical agitation such that sedimentation under gravity is not the predominating factor." Some authors have used this or a similar term with reference to the ability of solutions to retain solid particles in suspension under static conditions, and, while it is probable that there is some relationship between these two properties, complete agreement is not to be expected.

Some measurements of soil deposition on fabric, similar to those of the present paper, have also been reported but these have been concerned largely with noncarbonaceous soils (15, 17) or with synthetic detergents (11, 23, 24). Carter (2) carried out measurements of this type on various builders and soap-builder mixtures using a wide variety of soils including carbon black, and Vaughn and Vittone (25) reported somewhat similar work using as their soiling agent the carbon Norit C impregnated with Crisco and lubricating oil.

Broadly speaking the results of all these investigations indicate that silicate and phosphate builders either alone or in conjunction with soap are superior to sodium hydroxide, sodium carbonate, or other simple electrolyte builders as suspending agents for the majority of soil types, but there are wide differences in the data obtained with various soiling agents. As far as can be ascertained no work has been reported previously dealing with the suspending power with respect to carbonaceous soil of various builders in conjunction with pure soaps.

Materials and Methods

The method employed for the measurement of suspending power has been described in detail previously (29). The procedure consisted essentially of measuring photometrically the decrease in whiteness of pieces of cotton fabric after shaking for 20 min. in a suspension composed of carbon black (Standard Micronex), and the aqueous detergent solution. Owing to the high degree of deposition obtained with solutions containing alkaline builders, the weight of carbon used in each test was reduced from 0.25 gm., as used previously, to 0.125 gm.

Each experimental value recorded was obtained by averaging at least eight reflectometer readings. The per cent suspending power was calculated as follows:

$$\text{Suspending power } \% = \frac{B - B_w}{B_0 - B_w} \times 100,$$

where B = average reflectance of fabric at end of experiment,

B_w = "water value" (i.e., average reflectance of the fabric after shaking in a suspension of the carbon in distilled water),

B_0 = original reflectance of white fabric.

On this basis a suspending power of 100% represents no deposition of carbon on the fabric, and 0% represents the suspending power of distilled water. Negative values represent a suspending power less than that of distilled water.

The soaps used were prepared as indicated in the previous paper (29).

The following compounds also were used:

Sodium hydroxide	} Reagent grade
Sodium carbonate	
Sodium bicarbonate	
Sodium chloride	

Modified soda—a 1:1 molar ratio of sodium carbonate and sodium bicarbonate.

Sodium metasilicate—"Metso, granular" obtained from National Silicates Limited.

Na_2O , 29.4%; SiO_2 , 28.3%; ratio $\text{Na}_2\text{O}:\text{SiO}_2 = 1.01:1$.

Sodium sesquisilicate—"Metso 99", obtained from National Silicates Limited.

Na_2O , 36.9%; SiO_2 , 24.0%; ratio $\text{Na}_2\text{O}:\text{SiO}_2 = 1.49:1$.

Sodium orthosilicate—"Pensal", obtained from Canadian Industries Limited.

Na_2O , 61.5%; SiO_2 , 29.1%; ratio $\text{Na}_2\text{O}:\text{SiO}_2 = 2.04:1$.

Trisodium phosphate—"Fines" grade, Erco brand, obtained from Electric Reduction Company, Buckingham, Quebec.

Tetrasodium pyrophosphate—Obtained from Electric Reduction Company, Buckingham, Quebec.

Sodium hexametaphosphate—"Calgon" unadjusted, obtained from Charles Tennant (Canada) Ltd., Toronto, Ontario.

Stock 0.5% solutions of the various soaps and builders were prepared and diluted to the desired concentration immediately before use.

Suspending Power of Soap-builder Solutions

Measurements were made of the suspending power of solutions containing 0–0.1% of each of the builders, both alone and in the presence of 0.1% of sodium laurate, sodium stearate, and sodium oleate. Because of the limited solubility of sodium stearate, measurements involving the use of this soap were carried

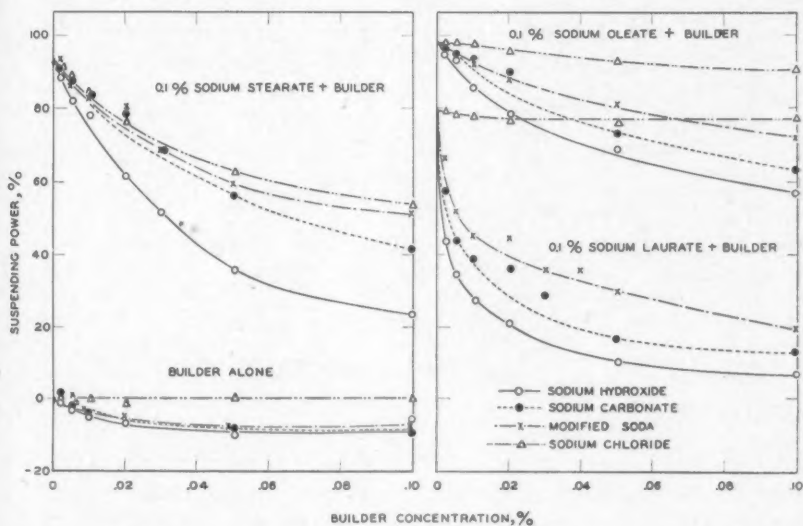


FIG. 1. Suspending power of builders of the simple electrolyte group. Temperature: laurate and oleate, 80°C.; stearate, 80°C.

out at 80°C., all other suspending power measurements being at 60°C. The data for sodium stearate are, therefore, not directly comparable with those for the other soaps. The results are shown graphically in Figs. 1, 2, and 3.

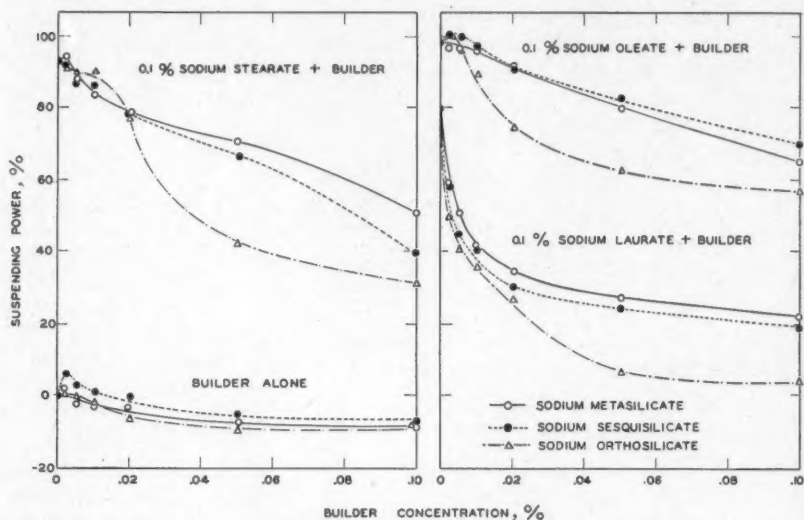


FIG. 2. Suspending power of builders of the silicate group. Temperature: laurate and oleate, 60°C.; stearate, 80°C.

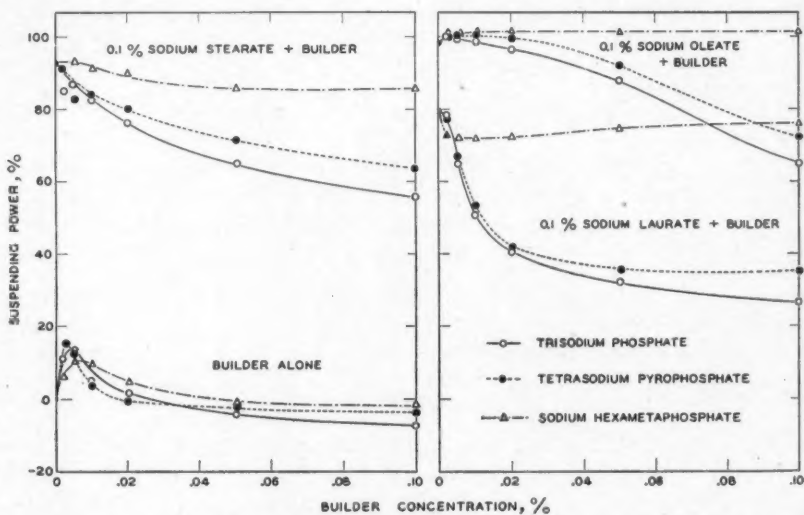


FIG. 3. Suspending power of builders of the phosphate group. Temperature: laurate and oleate, 60°C.; stearate, 80°C.

Another series of measurements was carried out in which fixed sodium stearate concentrations of 0, 0.01, 0.05, and 0.1% were used together with varying concentrations of sodium orthosilicate. These results are given in Fig. 4.

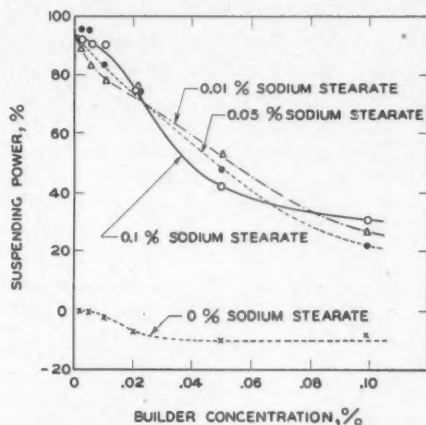


FIG. 4. Suspending power of sodium stearate-sodium orthosilicate solutions. Temperature: 80°C.

In a third series of experiments a fixed builder concentration of 0.05% sodium carbonate was used together with varying concentrations of sodium laurate, sodium myristate, and sodium stearate (Fig. 5).

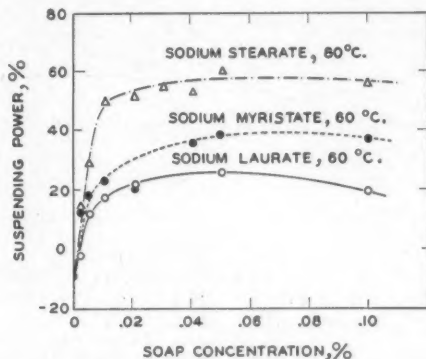


FIG. 5. Suspending power of various soaps in the presence of 0.05% sodium carbonate.

The pH of Soap-builder Solutions

The pH values of solutions containing a fixed concentration of soap and varying concentrations of each builder were determined at $70^{\circ}\text{C.} \pm 0.2^{\circ}$. The pH readings were made with a Beckman pH meter, Model G, using external glass electrode #1190. The electrode was calibrated against 0.05 M potassium

acid phthalate at 70°C. in accordance with the formula given by Bacon, Hensley and Vaughn (1), the instrument readings being corrected for temperature errors according to the formula given by Dole (5).

During the course of preliminary experiments it was observed that thermal shock resulting from removal of the electrodes from the thermostat and washing in cold water caused some change in the asymmetric potential calibration of the electrode. In order to overcome this difficulty the following apparatus was devised. A length of small bore glass tubing was sealed to the bottom of a 150 ml. beaker and bent as shown in Fig. 6, the bottom of the beaker being

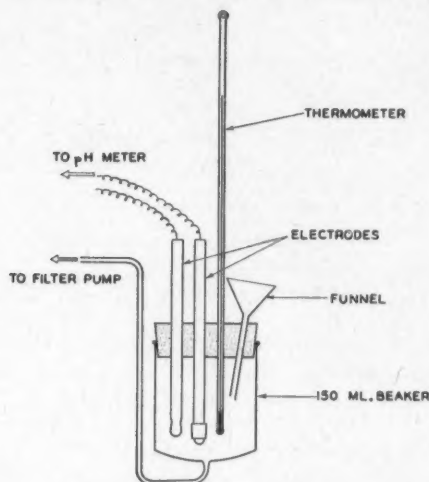


FIG. 6. *Modified apparatus for pH measurement.*

drawn out slightly to ensure complete drainage. The beaker was fitted with a rubber stopper carrying the two electrodes, a thermometer, and a funnel. The beaker was filled through this funnel and drained by means of the filter pump. The whole assembly was immersed in a thermostatically controlled water bath to within 1/4 in. of the top of the beaker. By the use of this apparatus the electrodes were maintained at 68–70°C. at all times, washing of the electrodes being effected by the addition of several consecutive portions of distilled water at 70°C. through the funnel.

In order to test the efficacy of this apparatus, the electrode was calibrated against the buffer solution, and a series of seven readings were made on soap solutions of varying concentration, the electrodes being washed as indicated above after each reading. At the end of this series a second portion of buffer solution was introduced and it was found that there had been no change in the asymmetric potential calibration, whereas when the electrodes were removed and rinsed with cold water between readings, changes in the calibration amounted to 0.2–0.4 pH units.

The method is also more rapid, since less time is required to attain thermal equilibrium.

Carbon dioxide-free water was used, since it was found that the presence of carbon dioxide influences the pH of soap solutions, although this effect appeared to be negligible in the presence of alkaline builders.

Solutions were prepared containing 0.1% soap and 0-0.1% builder. The results obtained are given in Table I.

TABLE I
pH OF SOAP-BUILDER SOLUTIONS AT 70°C.

Soap	None			Sod. laurate			Sod. stearate			Sod. oleate		
Builder	Builder concentration, %											
	0.01	0.05	0.1	0.01	0.05	0.1	0.01	0.05	0.1	0.01	0.05	0.1
None	6.93 (water)			8.44 (0.1% NaL)			9.63 (0.1% NaSt)			8.96 (0.1% NaOl)		
NaOH.....	10.12	10.59	10.63	10.00	10.43	10.42	9.96	10.42	10.43	9.74	10.27	10.50
Na ₂ CO ₃	9.68	10.08	10.14	9.61	9.94	9.96	9.74	9.83	9.90	9.39	9.88	9.83
Mod. soda	9.32	9.69	9.74	9.25	9.66	9.69	9.70	9.71	9.68	9.32	9.59	9.66
NaCl	6.99	6.89	6.89	8.47	8.38	8.13	9.59	9.43	9.37	8.89	8.80	8.78
Sod. metasilicate	9.60	10.12	10.26	9.47	9.99	10.13	9.84	10.02	10.18	9.14	9.89	10.10
Sod. sesquisilicate	9.64	10.20	10.30	9.58	10.18	10.27	9.84	10.15	10.27	9.37	10.17	10.27
Sod. orthosilicate	10.01	10.36	10.37	9.83	10.28	10.29	9.96	10.34	10.35	9.73	10.32	10.35
Trisodium phosphate	9.24	9.92	10.12	9.31	9.87	10.07	9.73	9.84	10.01	8.61	9.48	9.90
Tetrasodium pyrophosphate	9.19	9.53	9.58	9.14	9.45	9.51	9.66	9.58	9.47	8.55	9.04	9.20
Sodium hexameta- phosphate	7.78	7.95	7.79	8.23	7.91	7.74	9.67	9.41	9.08	8.29	8.10	7.94

The values recorded are somewhat lower than those usually associated with the various soaps and builders when measured at room temperature. This is due to the elevated temperature which results in a decrease in the pH value. The values for modified soda are in good agreement with those reported by Bacon, Hensley, and Vaughn (1) at the same temperature.

Discussion

In the absence of soap, none of the builders studied showed any marked ability to prevent the deposition of carbon particles on the fabric. In some cases suspending power maxima occurred at concentrations of 0.002-0.005%, the suspending power at higher concentrations falling off to values below that of distilled water. Even at this optimum concentration the suspending power of the builders was only slightly superior to that of distilled water and far below that of any of the soaps studied.

At first sight this appears to be contradictory to the findings of Fall (7), Carter (2), Powney and Nád (17), and others who claim a suspending power for sodium silicate solutions only slightly inferior to that of soap. However, the bulk of the work reported by these authors has involved the use of non-carbonaceous soils, and, according to Carter (2), the silicates are, in general, much less effective as suspending agents for carbonaceous soils than for other types. Since the water insoluble soils, of a visible nature, encountered in commercial laundering practice are most likely to be of the carbonaceous type, it would seem desirable to place the most weight on results obtained with this type of soil.

Except for a slight rise at low builder concentrations in some cases, the addition of increasing amounts of builder to soap solutions resulted in a progressive decrease in the suspending power of the solutions, this effect being less marked with the unsaturated soap, sodium oleate, than with the saturated soaps. The only exception to this general rule occurred in the case of solutions containing sodium oleate and sodium hexametaphosphate, where at all concentrations of the phosphate the suspending power was slightly higher than that of the unbuilt sodium oleate.

When the suspending power of the various built soap solutions at any given builder concentration (e.g., 0.1%) is plotted against the pH of the corresponding solution, it may be seen that the builders fall into three classifications, viz., simple electrolytes (i.e., sodium hydroxide, sodium carbonate, modified soda, and sodium chloride), silicates, and phosphates (Fig. 7). While there appears to be no general correlation between pH and suspending power, nevertheless there is a definite indication that, within each of these three groups, the suspending power improves with decreasing pH of the solution.

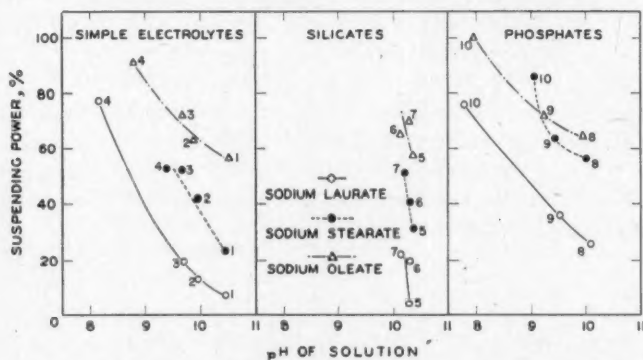


FIG. 7. Effect of pH on the suspending power of built soap solutions. The solutions contained 0.1% of the indicated soap + 0.1% of the following builders:

- | | |
|-------------------------|------------------------------|
| 1. Sodium hydroxide | 6. Sodium sesquisilicate |
| 2. Sodium carbonate | 7. Sodium metasilicate |
| 3. Modified soda | 8. Trisodium phosphate |
| 4. Sodium chloride | 9. Tetrasodium pyrophosphate |
| 5. Sodium orthosilicate | 10. Sodium hexametaphosphate |

Temperature: laurate and oleate, 60°C.; stearate, 80°C.

This work was repeated using ilmenite as the suspended material, and essentially similar results were obtained in so far as the relative order of suspending power within each of the three builder classifications was concerned. In this case, however, less pronounced differences were observed between the various builders, and the suspending powers of solutions containing sodium oleate were found to be somewhat inferior to those of solutions containing sodium stearate. The latter observation is not in agreement with the results obtained with Standard Micronex (29), but is, in general, confirmed by the work of Powney and Noad (17), who also used ilmenite as their suspended material.

Other investigators do not seem to have noted any marked differences between builders of the simple electrolyte group, with respect to their effect on the suspending power of soap solutions, although Powney and Noad (17) noted that the addition of sodium hydroxide or sodium carbonate to solutions of sodium oleate depressed the suspending power to a greater extent than did sodium chloride. They attribute this effect to a suppression of the formation of acid soap produced by hydrolysis which they believe exerts a greater protective action than the simple soap ion.

On the other hand, Tomlinson (22) in studies of the detergent action of a mixed fatty acid soap involving the washing of artificially soiled fabric observed a minimum in detergent action at a concentration corresponding approximately to that of maximum hydrolysis of the soap. Since this minimum was not observed with nonhydrolyzing synthetic detergents, and was removed by the addition of alkalis to the soap solution, Tomlinson concludes that at the concentration of maximum hydrolysis acid soap is adsorbed by the fabric, and physically prevents the removal of the underlying soil, and also denudes the solution of detergent molecules.

If both of these explanations are correct, it follows that the presence of acid soap is desirable from the standpoint of suspending power efficiency, but undesirable on the basis of soil removal efficiency. This may account for the diversity of opinions expressed in the literature (3, 12, 13, 16) regarding the role of acid soap in the detergent process. Such an hypothesis is not untenable if it is assumed that the hydrophobic carbon particles form nuclei about which the acid soap aggregate is built up. The carbon particle with its adsorbed film of acid soap would therefore have a high negative charge as a result of which its deposition on the negatively charged fabric would be diminished owing to electrostatic repulsion.

In the silicate group the more siliceous (or less alkaline) silicates show the highest suspending power. The differences are somewhat exaggerated owing to the fact that the three silicates contain varying amounts of water, but comparison on the basis of weight of anhydrous salt does not change the relative order of performance. This order is in accord with the findings of Fall (7), Carter (2), and Powney and Noad (17), although these authors reported a higher degree of suspending power for the silicates than has been found in the

present study. This discrepancy may be explained by the fact that the previous investigators used noncarbonaceous soils against which the silicates are more effective, and more highly siliceous silicates than those of the present work.

Powney and Noad (17) attribute the difference between the suspending powers of simple electrolytes and highly siliceous silicates in the absence of soaps to a difference in adsorption behavior. With simple electrolytes the sodium ion is preferentially adsorbed, causing a reduction in the negative charge carried by the soil particles, with a resulting reduction in suspending power. With the silicates a preferential adsorption of the anion is postulated, resulting in increased suspending power. It is not surprising that the strongly alkaline silicates behave in a manner more nearly resembling the simple electrolytes than the highly siliceous silicates. The results of the present study are, therefore, not necessarily at variance with the findings of earlier investigators in view of the differences in experimental technique and materials used.

In the phosphate group the less alkaline members also show the highest suspending power, sodium hexametaphosphate being much superior to the other phosphates. The higher suspending power of the less alkaline phosphates is again probably due to selective adsorption of the anion.

It has been shown (19, 27) that carbon preferentially adsorbs the fatty acid constituent of soap. This indicates that either free fatty acid or acid soap is adsorbed more readily than neutral soap by the carbon. This view is confirmed by the work of Fromageot and Wurmser (9) who found that the adsorption on charcoal of a wide variety of organic acids was always greater than the adsorption of the corresponding sodium salts. It has also been shown that suppression of soap hydrolysis by the addition of alkali to the solution resulted in a decrease in the adsorption of fatty acid by both carbon particles (27) and textile fibers (28). The action of alkaline builders in depressing the suspending power of soap solutions may therefore be attributed, at least in part, to a decrease in the adsorption of soap by the soil particles and by the textile fibers. This view is substantiated by the fact that the more alkaline builders, which would suppress soap hydrolysis to the greatest extent, also cause the greatest reduction in the suspending power of soap solutions.

Fig. 4 indicates that the suspending power of a built soap solution is more dependent on the concentration of the builder than on either the soap concentration or the soap-builder ratio, i.e., the effect of the builder predominates over the effect of the soap even when the ratio of soap to builder is relatively high, provided that a certain minimum concentration of soap is present. In the complete absence of soap the suspending power is of course very low. Fig. 4 also shows very clearly that the suspending power of a built soap solution, as measured by the present technique, is equivalent to neither the sum nor the average of the suspending powers of the ingredients when used separately, as has been assumed by some workers (7, 20).

While the soap concentration (within certain limits) is relatively unimportant in so far as its effect on the suspending power of built soap solutions is concerned, the type of soap used has a considerable influence (Fig. 5), the higher suspending power being obtained with the longer chain soaps.

In attempting to classify the builders according to their effect on the suspending powers of soap solutions, it was found that the order of merit varied, not only with the particular soap considered, but also with the soap-builder ratio at which the comparison was made. In actual practice the effective soap-builder ratio is likely to be influenced by such factors as the hardness of the

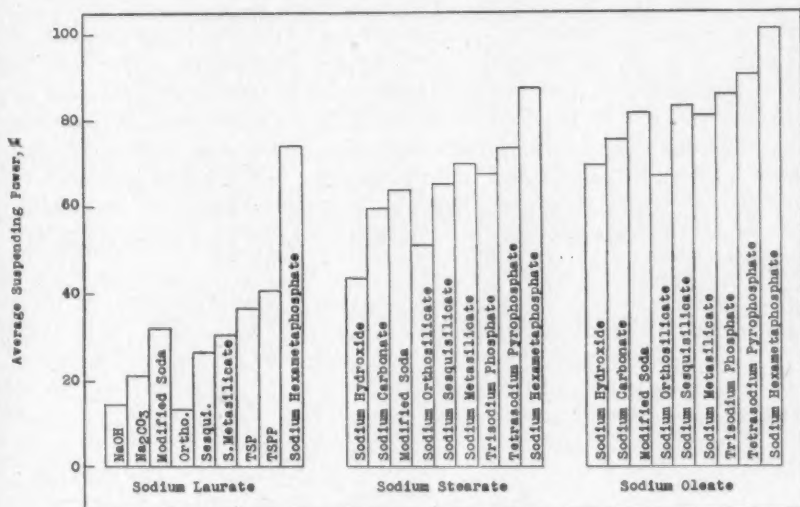


FIG. 8. Classification of builders on the basis of suspending power. Temperature: laurate and oleate, 60°C.; stearate, 80°C.

water, acidity in the load, and adsorption by both fabric and soil. Consequently a more useful classification can be obtained by comparing the average suspending powers over a range of soap-builder ratios. A comparison of builder efficiencies was made on this basis by measuring with a planimeter the areas under the curves of Figs. 1, 2, and 3, and calculating the average suspending power for each built soap solution over the builder concentration range 0–0.1%. Sodium chloride was omitted from this classification, since it cannot properly be included with laundry soap builders. The results are given in Fig. 8, which gives an indication of the over-all efficiency of the various built soap solutions with respect to suspending power. The marked superiority of sodium hexametaphosphate is clearly shown, while sodium hydroxide and sodium orthosilicate have the lowest suspending powers. The remaining builders fall into a single group with only minor differences between them.

In any attempt to classify builders according to their efficiency as suspending agents it must be remembered that all the builders, with the possible exception of sodium hexametaphosphate, cause a decrease in the suspending power of the unbuilt soap. Yet builders are known to have an over-all beneficial effect in the detergent process (4). In detergent operations in which water of appreciable hardness is used this beneficial effect is understandable, since the builders are known to have water softening ability (8). However, experience has shown that in soft water such as is used in commercial laundry practice, builders may also be used to advantage, both from the standpoint of soap economy and improved detergency, and that various builders differ in their effectiveness in these respects. Some of this effect is undoubtedly due to the saponification of fatty acids present in the fabrics being laundered and to the known powerful effect of "nascent" soaps (18) in facilitating the removal of soil from the areas in which the saponification occurs; but the capacity to effect such saponification would be similar with builders having alkalinities above a certain minimum value. Hence the known effectiveness of a builder such as sodium metasilicate as compared with that of sodium hydroxide cannot be attributed to differences in ability to saponify fatty acids; but it could well be related, in part at least, to the differences in ability to suspend solid soils as shown in the present and other work.

Many authors (10, 17, 26) have concluded that suspending power depends largely on the magnitude of the charges carried by the soil particles as a result of the adsorption of ions. Work recently reported by Doscher (6), however, tends to indicate that this assumption is only partially correct. Doscher found a reasonable correlation between the electrophoretic mobility of carbon particles in solutions of Hyamine 1622 (a cationic agent) and suspendibility of the carbon in the same solutions up to concentrations of about 0.4%. At higher concentrations, however, the suspendibility decreased whereas the mobility continued to increase slightly. Furthermore, solutions of Renex (a nonionic agent) at concentrations varying from 0-5% had little or no effect on the mobility of the carbon, yet these solutions were shown to have considerable suspending power. Doscher suggests that "it is not the change in zeta potential, per se, which gives rise to suspendability or detergency, but whether or not the detergent can be adsorbed on dirt and fabric, in ionized or non-ionized form, and the resulting nature of the exposed surfaces—whether hydrophobic or hydrophilic." Thus it appears that the mechanism of suspending action is even more complex than has been assumed previously, and that, in addition to the effects of electrostatic repulsion which are probably operative at relatively low concentrations of ionizing detergents, there is also the effect of the nature of the exposed surfaces, which may predominate in higher concentrations of ionizing detergents and in all concentrations of nonionizing detergents.

While the precise mechanism of suspending action is thus somewhat in doubt, nevertheless it is apparent that suspending power is closely related to, and influenced by, the adsorption of ions and/or micelles of the detergent compound at the various interfaces concerned.

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THE EFFECT OF HEMICELLULOSES ON THE PAPERMAKING PROPERTIES OF WHITE BIRCH¹

By D. A. SITCH AND H. BORDEN MARSHALL

Abstract

A fibrous holocellulose was isolated from white birch using hot acidified sodium chlorite solutions. Pulps of varying hemicellulose content were prepared by alkaline treatment, and their beating and sheetmaking properties compared with the original holocellulose. Tensile strength increased with hemicellulose content, whereas tearing resistance and fold endurance decreased. Bursting strength reached a maximum at about 15% alkali-extractable hemicellulose content. Pulps obtained in yields of 46-53%, i.e., containing 10-20% hemicellulose, possessed the best over-all strength.

A bleached sulphite pulp prepared from the same chips in a yield of 43.6% contained 20.7% alkali-extractable hemicellulose. The over-all yield of α -cellulose was about 6% lower, based on the wood, than in the case of the holocellulose, thus indicating greater fiber damage during the sulphite process. Hand sheets made from the sulphite pulp were inferior to sheets made from a chlorite pulp of the same hemicellulose content in bursting and tensile strengths but had better tearing and fold properties.

The presence of hemicellulose was found to increase the rate at which the average fiber length was reduced during beating, thus indicating a correlation between fiber flexibility and hemicellulose content.

Since pulps of high strength were prepared, it was concluded that greater quantities of white birch pulp at the appropriate hemicellulose content could be incorporated in many commercial furnishes.

Introduction

It is becoming increasingly necessary to utilize more fully the hardwood resources of Canada. The chief objection to the greater use of these species by the pulping industry is that the strength of the finished paper is low compared with that made from the conventional softwoods (14). This disadvantage has been mainly attributed to their shorter fibres. Before increased utilization is possible, methods must therefore be found to improve the over-all strength of sheets made from the hardwoods. This would allow the use of a greater percentage of these species in any given furnish. However, the fundamental physical properties of hardwood fibres are such that only in a few cases can they be used as 100% furnish (4, 14).

The important role of hemicelluloses in pulp processing and papermaking has been increasingly recognized during the past decade (5, 6, 9, 10, 12, 17, 18). Some excellent reviews of this field have been published (13, 26, 27). The general conclusion that has been reached by earlier workers is that a stronger pulp can be obtained by adjusting cooking and bleaching procedure to secure greater hemicellulose retention at the same lignin content. There is also much evidence to indicate that there may be an optimum hemicellulose content for maximum pulp strength, i.e., if pulps are obtained with too high a hemicellulose content, sheet strength is reduced (9, 11, 13).

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The first step towards increased utilization of hardwoods by the pulping industry is the determination of the optimum pulping conditions necessary to secure maximum strength. This investigation was therefore designed to determine the effects of hemicellulose content on the strength of pulps made from one of these species, viz., white birch.

This type of problem has been studied by introducing hemicellulosic materials into pulps of high α -cellulose content whilst in the beater and determining the effect on the strength of the resultant sheets (10, 13, 16). However, the unknown physical and chemical changes that occur during the isolation of the hemicellulose from the wood probably reduce its efficacy. Furthermore, the retention of hemicellulose by the beaten pulp is poor (13, 16).

A better approach to this problem is the investigation of a series of pulps from which varying amounts of the original hemicellulose have been removed. This can be accomplished by preparing a "holocellulose" pulp, and then isolating from this pulp a series of residues containing varying proportions of hemicellulose. The behavior of each of these materials during beating and the physical properties of handsheets made therefrom can then be studied. This approach has been used by Houtz and Kurth (7) for spruce and recently, whilst the present investigation was in progress, by March (13) for aspen.

Methods of delignifying wood to yield holocellulose have been discussed previously (19). The Van Beckum and Ritter procedure of chlorination followed by ethanolamine extraction (22, 23, 24, 25) has been used to prepare fibrous holocellulose from white spruce Asplund fiber (6) and from thin spruce shavings (7). Unfortunately, this method is not suitable for use with chips, as poor chlorine penetration results in an excessive proportion of screenings. However, the procedures of Jayme (8) and of Wise *et al.* (28, 29) involving delignification with hot acidified chlorite solutions are readily applicable to the pulping of chips (12, 13).

The extraction of hemicellulose from fibrous holocellulose can be accomplished with aqueous caustic alkali (13, 15, 21, 28, 29). The use of organic bases does not apparently present any advantages (20). However, the possibilities of alkaline oxidation must be reduced to a minimum by excluding air during the extraction (28). In this way, the original α -cellulose content of the wood is preserved intact and the resulting pulps differ only in hemicellulose content.

Accordingly it was decided to isolate a white birch holocellulose by the chlorite procedure and then to prepare residual pulps from this material by alkaline extraction under nitrogen.

Experimental and Results

Raw Materials and Methods of Analysis

A sound log of white birch (*Betula papyrifera* Marshall), age 29 years, was stripped and chipped. The chips were hand-sorted; only those between 1/2 in. and 1 in. long and up to 1/4 in. thick were retained.

Standard Tappi methods of analysis* were employed for lignin, α -cellulose, and pentosan. However, no correction was made in the pentosan determinations for the production of hydroxymethylfurfural from the cellulosic constituents present, and a yield of 92.5% furfural from pentose was assumed (based on results obtained from xylose). In no cases have pentosan values been corrected for the furfural obtained from any hexuronic acids present.

The Pulping of White Birch Chips by the Chlorite Method

The chips were pulped with acidified chlorite solution (8, 28) and in order to obtain complete defibration it was found necessary to remove some of the hemicellulose (approximately 9% of the original). This was accomplished by prolonging the treatment.

Delignification of 3,682 gm. air-dry chips (15.4% moisture) was carried out in a 10 gal. crock according to the schedule given in Table I. In each treatment

TABLE I
CHLORITE COOKING SCHEDULE

Treatment, No.	Consistency, %	* Sodium chlorite, gm.	pH	Maximum temp., °C.
1	23	1645	5.0	75
2	26	1850	5.0	75
3	26	1390	5.0	75
4	12.5	700	5.0	60
Screenings	ca. 7	200	5.0	75

* Technical grade.

direct steam heating was used over a period of 1 1/2 hr. to raise the temperature of the cook gradually to the value shown. The steam was then shut off and the cook allowed to cool overnight to room temperature. At the end of each treatment, the chips were drained on a coarse screen, returned to the crock, fresh liquor added, and the pH adjusted to 5.0 before heating was commenced. The pH of the liquors did not change appreciably during any one treatment. After the fourth treatment the softened, pale-yellow chips were disintegrated in water with a high speed propeller-type stirrer and the resultant stock flat screened using a 0.010 in. cut plate. As the proportion of screenings (ca. 500-700 gm.) was considered excessive they were treated with fresh chlorite solution, disintegrated once more, and rescreened.

The cooked pulp (pulp 1) was well washed with water, collected on a 100 mesh screen, and air-dried. Yield on an O.D. basis: screened pulp, 63.6%; screenings, 1.7%.

The following analysis (corrected for 1.0% ash) was obtained for the screened pulp: lignin, 2.7%; pentosan, 24.05%; and α -cellulose, 62.6%. It was considered that this pulp contained the maximum amount of hemicellulose con-

* The standard testing methods of the technical association of the pulp and paper industry.

sistent with complete chip disintegration and was therefore suitable for the preparation of four pulps of varying hemicellulose content.

The Extraction of Hemicellulose from Chlorite Pulp

Small scale extractions were first carried out with a variety of alkali concentrations in order to investigate the relation between alkali strength and the proportion of hemicellulose extracted. Concentrations were then selected such that a series of pulps could be obtained with hemicellulose contents differing by a uniform interval.

The large scale extractions were done in crocks, using liquors made up with boiled tap water. In the first extraction chlorite pulp (1625 gm., O.D. basis) was slurried at a consistency of 4.4% in 0.05% potassium hydroxide. The mixture was maintained at a temperature of $25 \pm 1^\circ\text{C}$. for 1 1/2 hr. with frequent stirring. The pulp was then drained on a 100 mesh screen, returned to the crock, and the extraction repeated under the same conditions. After extraction, the pulp was washed well with water, dilute acetic acid (ca. 0.1%), and finally with water. It was then air-dried, weighed, and the moisture content determined (pulp 2).

Pulp 2 was divided into four portions. The first portion (345 gm., O.D. basis) was extracted twice at a consistency of 2.6% under the same conditions as given above except that 0.3% potassium hydroxide was used. Approximately 1% acetic acid was employed in the washing process. The yield (pulp 3) was determined as described above.

A second portion of pulp (385 gm., O.D. basis) was slurried in 13 liters of 0.5% potassium hydroxide and allowed to stand at 25°C . for 30 min. under nitrogen. The appropriate amount of a stronger alkali solution (6.2 liters of 8.24%) was then added to adjust the concentration of potassium hydroxide to 3.0% and the consistency to 2.0%. The suspension was then allowed to stand at 25°C . for a further period of one hour. During this time the pulp was continuously stirred under a blanket of nitrogen. The bulk of the extraction liquor was then drained off and the pulp re-extracted with 3.0% potassium hydroxide for 1 1/2 hr., the initial weak alkali treatment being omitted. The residual pulp was collected on a 100 mesh screen, washed with water, 5% acetic acid, and again with water (pulp 4).

The third portion of pulp 2 (451 gm., O.D. basis) was treated by the procedure described above using 13 liters of 1.0% potassium hydroxide for the initial swelling process and 22.5 liters of 10% potassium hydroxide for each extraction (pulp 5).

The final portion of pulp 2 was retained for beater evaluation and chemical analysis. The analytical data for these pulps are shown in Table II.

Since the α -cellulose content of pulps 2-5, based on the original wood, was in each case between 40 and 43%, and the viscosity of these pulps increased with decreasing hemicellulose content, it seemed probable that little degradation had occurred during the alkaline extractions.

It was considered that these materials differed sufficiently in pentosan and α -cellulose content to be suitable for the determination of the effect of hemi-cellulose on paper properties.

TABLE II
THE ANALYSES OF CHLORITE PULP BEFORE AND AFTER ALKALINE EXTRACTIONS

Pulp	Concn. of KOH used in extraction, %	Yield of pulp based on wood,* %	Pentosan content, %	α -Cellulose content, %	Viscosity,** cp.
1	Original chlorite pulp	65.3	24.05	62.6	12.1
2	0.05	60.7	22.0	70.5	12.0
3	0.05 & 0.3	52.2	18.8	82.6	14.5
4	0.05 & 3.0	46.2	12.8	89.1	15.2
5	0.05 & 10.0	41.8	3.8	95.1	19.55

* Including screenings.

** Tappi T290 (27); 0.5% solution in 0.5M cupriethylene diamine, using Ostwald pipettes.

Beating Procedure

Beating tests were carried out according to Tappi Standard Method T200 using a 1 1/2 lb. Valley beater, and about 300 gm. (O.D. basis) of pulp at 1.57% consistency. A beater arm load of 4.5 kgm. was employed. Withdrawals for freeness tests (Tappi T227) and hand sheets (10 sheets, Tappi T205) were made at intervals of 10-30 min. depending on the type of pulp and the extent of beating. The first withdrawal was usually made after five minutes' beating to ensure disintegration of any residual fiber bundles.

TABLE III
THE PHYSICAL PROPERTIES OF SHEETS MADE FROM CHLORITE PULP 1
(Moisture content of air-dry pulp = 13.3%)

Beating time, min.	Freeness, (Canadian Standard), ml.	Basis weight, gm./sq. m.	Bulk, cc./gm.	Tear factor, 100 X gm./gm.	Burst factor, gm./sq. cm./gm.	Breaking length, m.	Fold endurance, double folds
5	538	61.8	1.38	71	53	10,000	320
15	368	58.25	1.29	60	64.5	10,700	450
25	186	58.4	1.22	56	67	11,600	680
37	43	59.1	1.13	48	71	11,700	900
52	4	59.55	1.13	41	66	11,900	510

TABLE IV
THE PHYSICAL PROPERTIES OF SHEETS MADE FROM CHLORITE PULP 2
(Moisture content of air-dry pulp = 23.9%)

Beating time, min.	Freeness, (Canadian Standard), ml.	Basis weight, gm./sq. m.	Bulk, cc./gm.	Tear factor, 100 X gm./gm.	Burst factor, gm./sq. cm./gm.	Breaking length, m.	Fold endurance, double folds
5	593	53.9	1.58	74	49.5	7800	280
15	436	53.55	1.485	63	62	9600	600
25	254	51.45	1.46	55	68	10,900	1000
40	67	52.5	1.30	53	71	11,300	1400
54	14	51.35	1.31	47	63.5	10,300	1400

TABLE V
THE PHYSICAL PROPERTIES OF SHEETS MADE FROM CHLORITE PULP 3
(Moisture content of air-dry pulp = 32.6%)

Beating time, min.	Freeness, (Canadian Standard), ml.	Basis weight, gm./sq. m.	Bulk, cc./gm.	Tear factor, 100 × gm./gm.	Burst factor, gm./sq. cm./gm.	Breaking length, m.	Fold endurance, double folds
5	626	59.2	1.40	71	41	6500	220
15	509	56.6	1.28	83	57	8450	580
30	285	55.3	1.21	60	70	10,500	1000
45	143	52.9	1.185	57	80	11,300	1700
65	12	48.9	1.27	63	90.5	12,100	2000

TABLE VI
THE PHYSICAL PROPERTIES OF SHEETS MADE FROM CHLORITE PULP 4
(Moisture content of air-dry pulp = 41.8%)

Beating time, min.	Freeness, (Canadian Standard), ml.	Basis weight, gm./sq. m.	Bulk, cc./gm.	Tear factor, 100 × gm./gm.	Burst factor, gm./sq. cm./gm.	Breaking length, m.	Fold endurance, double folds
5	652	59.4	1.33	116	27	4700	45
20	435	59.7	1.22	83	59	8700	1300
35	233	59.8	1.14	74	76	10,500	2000
50	75	59.9	1.07	73	78	11,300	3500
75	6	62.2	1.01	54.5	86	11,200	4100

TABLE VII
THE PHYSICAL PROPERTIES OF SHEETS MADE FROM CHLORITE PULP 5
(Moisture content of air-dry pulp = 6.6%)

Beating time, min.	Freeness, (Canadian Standard), ml.	Basis weight, gm./sq. m.	Bulk, cc./gm.	Tear factor, 100 × gm./gm.	Burst factor, gm./sq. cm./gm.	Breaking length, m.	Fold endurance, double folds
5	679	59.6	2.19	32.5	5	1300	1
20	641	—	—	—	—	—	—
30	—	55.9	1.74	99.5	19	3200	10
45	562	—	—	—	—	—	—
63	—	56.8	1.46	128	46	6100	600
75	379	—	—	—	—	—	—
90	285	53.6	1.36	117	57	7200	1700
120	177	57.3	1.30	107	70	8400	2400

The Physical Testing of Hand Sheets

Tappi Standard Methods (30) were used for conditioning the hand sheets and for the determination of thickness, weight, moisture content, burst factor, tear factor, tensile strength, and fold endurance. Tensile tests were made with a Scott Incline Plane machine (Model IP 4) and fold endurance measurements with a Schopper instrument.

The freeness results and physical test data obtained for pulps 1-5 are presented in Tables III to VII.

Pulps 1 and 2 gave "tinny" glassinelike sheets whilst those from 5 were soft and bulky. Sheets from 3 and 4 had intermediate properties.

The Sulphite Pulping of White Birch

For purposes of comparison a bleached sulphite pulp was prepared from the same batch of chips as was used for chlorite pulping. The cook was carried out in an indirectly heated stainless steel digester (0.8 cu. ft. capacity) using sodium base liquors under the following conditions:

Weight of chips (O.D. basis), gm.	2,250
Volume of liquor, liters	14.1
Free SO ₂ (based on liquor), %	5.70
Combined SO ₂ (based on liquor), %	1.48
Total SO ₂ (based on liquor), %	7.18
Time to 100°C., hr.	2
Time from 100–120°C., hr.	1 1/2
Time from 120–130°C., hr.	2 1/2
Time at 130°C., hr.	3
Time from 130–80°C., hr.	1
Maximum pressure (by relief), p.s.i.	75

After cooking, the softened chips were disintegrated with a high speed propeller-type stirrer. The resultant pulp was collected on a 100 mesh screen, washed well with hot water, and then flat screened over a 0.010 in. cut plate. Yield on an O.D. basis: screened pulp, 43.3%; screenings, 1.64%. Analysis of pulp: lignin, 5.9%; pentosan, 12.75%; α -cellulose, 79.4%.

The Bleaching of Birch Sulphite Pulp

Birch sulphite pulp (360 gm. O.D. basis) was immersed in water (5 liters at 70°C.). A solution of sodium chlorite (50 gm. in 2.5 liters) at pH = 5.0 was then stirred into the pulp suspension, the resultant pH being 5.3. After standing for 15 min., the color of the pulp had changed from pale red-brown to light yellow. The suspension was therefore diluted with 7 liters of water, filtered on a 100 mesh screen, and the pulp thoroughly washed with warm water. Yield: 97.2% (based on unbleached pulp). Analysis: lignin, 2.6%; pentosan, 12.8%; α -cellulose, 79.3%. Bleaching losses were thus accounted for almost entirely by the reduction in lignin content.

The Evaluation of Sulphite Pulp

The bleached sulphite pulp was processed in the Valley beater and hand sheets were made as described earlier. The results of the physical tests carried out on these sheets are given in Table VIII.

The Fiber Distribution of Chlorite Pulps at Various Degrees of Beating

A study was made of the effect of hemicellulose content on the rate of fiber breakdown in the beater. This was accomplished by determining the distribution of fiber lengths of pulps 1, 3, 4, and 5 at intervals during beating. In each case a volume of pulp calculated to contain about 12 gm. of fiber was withdrawn from the beater and filtered on a Büchner funnel. The resultant pulp cake was air-dried, weighed, and the moisture content determined. The air-dry pulp was then immersed in water and after standing overnight was

TABLE VIII
THE PHYSICAL PROPERTIES OF SHEETS MADE FROM BLEACHED BIRCH SULPHITE PULP
(Moisture content of air-dry pulp = 7.9%)

Beating time, min.	Freeness, (Canadian Standard), ml.	Basis weight, gm./sq. m.	Bulk, cc./gm.	Tear factor, 100 × gm./gm.	Burst factor, gm./sq. cm./gm.	Breaking length, m.	Fold endurance, double folds
0	698	58.0	2.12	34	5	1500	1
15	633	54.7	1.70	72	18	3600	13
30	523	54.8	1.51	95	35	6100	170
45	368	54.7	1.37	77	46	7900	1100
60	220	55.8	1.42	79	55	8300	1800
75	80	55.3	1.36	80	66	9000	3700

easily dispersed with an electric mixer. The suspension was divided into two equal portions and each fractionated with a Johnston screen classifier (1). Mean percentage distributions are given in Table IX.

TABLE IX
THE EFFECT OF BEATING ON FIBER DISTRIBUTION

Pulp	Beating time, min.	Fiber distribution, % by weight				
		> 28-mesh	28-48 mesh	48-100 mesh	100-200 mesh	<200 mesh + losses
1	5	3	53	26.5	5	11.5
	25	—	—	—	—	—
	52	6	22	43	9	20
3	0	5	67	18	4.5	6
	30	5	44	25.5	6	19
	65	8	18	39	8	27
4	5	5	68	17	4.5	5
	35	6	57	20	5	11
	75	11	18	17	10	44
5	5	8	65	19.5	*	7
	75	5	62	18	*	16
	120	6	53.5	21	*	20

* During the time pulp 5 was being fractionated the 200 mesh screen was blocked and was therefore not used.

Discussion

The Effect of Hemicellulose Content on Paper Strength

The data illustrate the influence of hemicellulose content on the behavior of these pulps during beating and on the strength of the resultant sheets. The rate at which freeness was lost in the beater was proportional to the hemicellulose content, e.g., the freeness of pulp 1 fell off very rapidly whereas pulp 5 proved difficult to beat. Pulps 3 and 4 developed bursting strengths that com-

pared favorably with average values found for commercial softwood pulps; similarly pulps 1 to 4 attained high tensile strengths. The tearing resistances of those pulps containing a high proportion of hemicellulose (pulps 1-3) were poor, whereas that of "high-alpha" pulp 5 was very good. With the exception of pulp 4 the fold endurance values were not unusually high.

The strengths of pulps 1-5 at a Canadian Standard Freeness of 200 cc. (obtained by interpolation) are compared in Figs. 1 and 2, on the basis of "alkali-

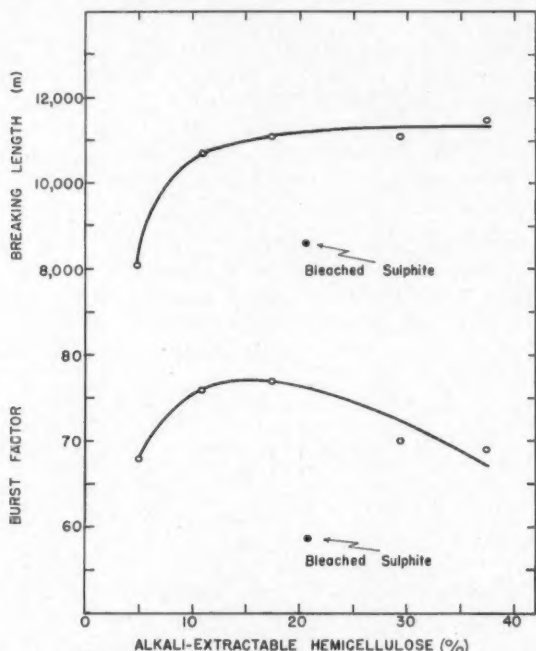


FIG. 1. The effect of hemicellulose on sheet strength: burst factor and breaking length (freeness 200 cc.).

extractable" hemicellulose, i.e., 100-% α -cellulose. This is considered to be a closer approximation of the hemicellulosic fiber-bonding material than the pentosan content, as the latter does not include hexosan hemicellulose, a component that undoubtedly takes part in fiber bonding.

The curves indicate that, in general, optimum strength was reached between 10 and 20% hemicellulose content (46 to 54% pulp yield), the exact percentage depending on the properties required in the finished sheet. Bursting strength increased to a maximum between 13 and 17% hemicellulose, whereas tensile strength increased continuously, the increase being quite marked up to 10% hemicellulose. By contrast both fold endurance and tearing resistance decreased

continuously, the reduction in tear being greatest between 5 and 12% hemicellulose.

In order to obtain a precise estimate of the degree to which sheet properties are influenced by the presence of hemicellulose it is necessary to compare sheets containing the same number of fibers and of the same degree of fiber-to-fiber

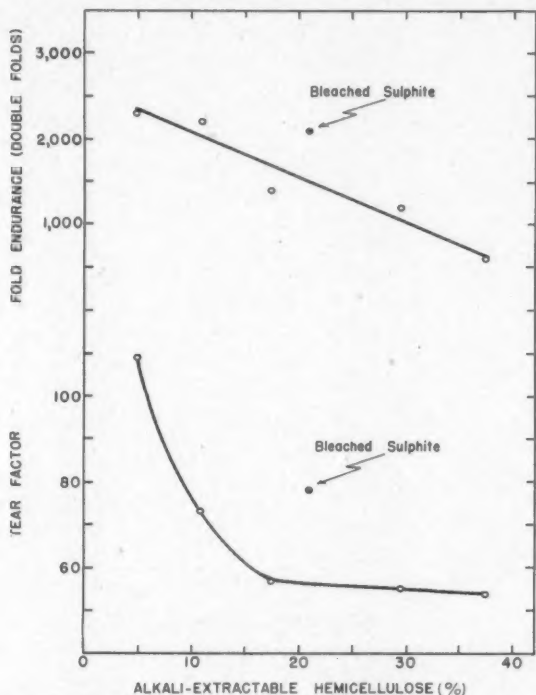


FIG. 2. The effect of hemicellulose on sheet strength: tear factor and fold endurance (freeness 200 cc.).

contact (2, 3). The results discussed above therefore indicate only the apparent effects of hemicellulose since the comparison has been made simply with sheets of the same basis weight according to normal practice. Although the fiber packing or degree of fiber contact can be controlled to some extent by the conditions of wet pressing of the sheets, this was not done in the experiments described above as the number of test runs to be carried out would have been greatly increased.

However, some indication of the relative strengths of sheets of the same fiber content may be obtained if the results are compared at the same α -cellulose content per sheet. Therefore the strength values of each pulp at 200 cc.

freeness were multiplied by the factor $100 \div \% \alpha$ -cellulose, and the results plotted against hemicellulose content (Figs. 3 and 4).

In contrast with the results expressed in Figs. 1 and 2, bursting and tensile strength increased much more uniformly with hemicellulose content, no

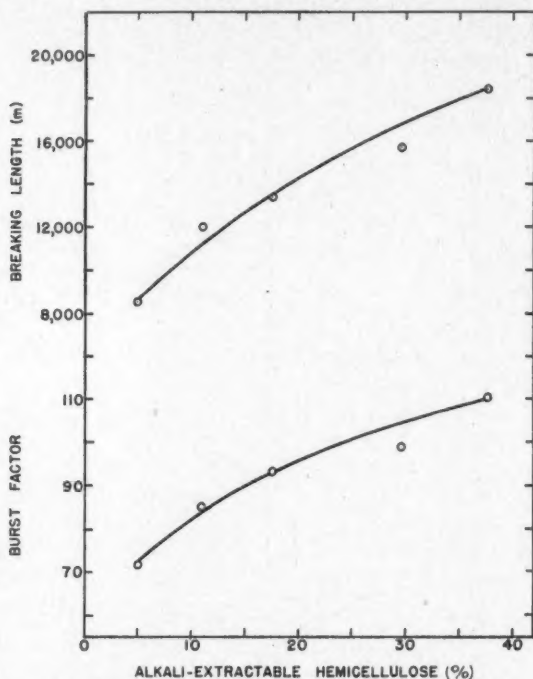


FIG. 3. The effect of hemicellulose on sheet strength: burst factor and breaking length (expressed on the basis of equal α -cellulose content at freeness 200 cc.).

maximum in burst being observed. It is thus apparent that even the holo-cellulose pulp did not contain sufficient hemicellulose to cause a reduction in fiber bond strength. Tear strength reached a minimum at 20% hemicellulose and fold decreased less rapidly than when expressed on the basis of equal sheet weight.

Properties of the Bleached Sulphite Pulp

The maximum tensile strength attained by the sulphite pulp was 20–25% lower than the maximum values for chlorite pulps 1–4 (see Tables III to VIII). This suggests that the fiber damage which occurred during sulphite cooking was considerably greater than that which took place during the chlorite delignification and subsequent extractions. In the latter pulps, fiber damage during the alkaline treatments appeared to be negligible since the yields of α -cellulose from all chlorite pulps were essentially the same, viz. 40–43% (see Table II). Furthermore, as the sulphite pulp contained only 35% α -cellulose

(based on the wood) it is apparent that about 15% of the original α -cellulose was sufficiently degraded during the sulphite cook, to be rendered soluble in 17.5% sodium hydroxide.

As shown in Figs. 1 and 2, the sulphite pulp at 200 cc. freeness was inferior in burst and tensile to a chlorite pulp of the same "alkali-extractable" hemicellulose content (20.7%) but had a higher tear and fold. It is doubtful if the hemicellulose formed by degradation of α -cellulose functions in precisely the

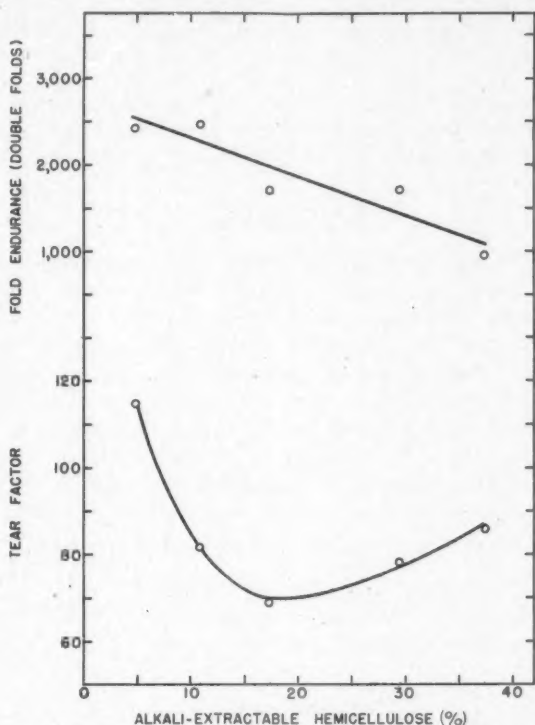


FIG. 4. The effect of hemicellulose on sheet strength: tear factor and fold endurance (expressed on the basis of equal α -cellulose content at freeness 200 cc.).

same manner during beating and sheet formation as the original hemicellulose. Hence a comparison with a chlorite pulp of the same "alkali-extractable" hemicellulose content is not entirely valid. Nevertheless, it is considered that the differences in strength discussed above were due mainly to degradation which occurred during the sulphite cook.

The Effect of Hemicellulose on Fiber Brittleness

The chlorite pulps possess approximately the same fiber length distribution in the relatively unbeaten state (Table IX). This indicates that the mechanical and chemical processes involved during the alkaline extraction did not appre-

ciably change this distribution. However, the effect of beating varied considerably from pulp to pulp. Those pulps which were rich in hemicellulose suffered greater fiber disintegration in a given time than those from which hemicellulose had been extracted. It thus appeared that fibers from which the hemicellulose had been substantially removed were more flexible and hence were less damaged during beating. The poor tearing properties of holocellulose-type pulps may therefore be the result of two effects, firstly, the more extensive reduction in fiber length which occurs as these pulps are beaten, and secondly, the greater brittleness of the individual fibers. These two effects thus tend to counterbalance any improvements brought about by the presence of hemicellulose.

It will also be noticed, that in the case of those pulps containing small percentages of hemicellulose, disintegration was accompanied by an increase in fines rather than an increase in the percentage of an intermediate fraction.

Conclusions

The proportion of hemicellulose allowed to remain in the pulp greatly influences certain properties, i.e., the rate at which freeness is reduced in the beater, the strength of the fiber-to-fiber bonds, and the flexibility of the fibers. By pulping under conditions that will result in the appropriate hemicellulose content any one of these properties can therefore be increased to the maximum possible extent. Unfortunately, the pulping method least likely to cause degradation and strength reduction, viz., chlorite delignification followed by alkaline treatment, is not commercially feasible. However, the degradative effects of such commercial cooking methods as the sulphite process could be reduced by suitable modification of conditions. Undoubtedly some of the semi-chemical processes would be successful in producing stronger pulps.

Since it has been shown in the above experiments that pulps of high strength can be prepared from white birch, it was concluded that greater quantities of this species could be incorporated in many furnishes.

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SEPARATION OF STARCH AND GLUTEN

V. PROBLEMS IN WHEAT STARCH MANUFACTURE ARISING FROM FLOUR PENTOSANS¹BY K. A. CLENDENNING² AND D. E. WRIGHT³

Abstract

The voluminous starch sludge or "squeegee" fraction, obtained with all known methods of wheat starch manufacture, consists of strongly hydrated pentosan masses in which starch granules are embedded. The pentosans of the bran and endosperm both contribute to the formation of these heterogeneous complexes. The "squeegee" starch fraction is not abolished by allowing the crude starch slurries to ferment, by exposing them briefly to mildly acid or alkaline solutions, or to C_2 - C_{12} monohydric alcohols. The pentosan and protein contents of this low quality starch fraction may be greatly reduced by 24-48 hr. digestion in dilute acid at pH 2.0 before recovering the starch on the centrifuge.

Introduction

Many recent publications have dealt with the separation of wheat starch and gluten. Publications from the Northern Regional Research Laboratory have described an adaptation of the corn wet-milling process (20), an alkali process (6), and the batter process (10). Earlier papers in the present series (I-IV) have dealt with a modified Martin process (1, 9) and the screening process (17-19). Lusena (11) has also described a method in which the gluten is dispersed mechanically in 0.005 *N* acetic acid; the crude starch is then recovered on the centrifuge, and "vital" gluten is recovered subsequently, either by adjusting the gluten solution to neutrality or by spray drying (11-13).

Industrial experience with the foregoing methods has been relatively unsatisfactory, with respect to the recovery of prime quality starch, in high yield, from crude starch slurries. This problem arises through the formation of slimy starch sludge fractions known in the trade as "squeegee" starch. When the crude starch slurry is held in settling tanks, only a fraction of the starch settles out as "hard" starch. When the slurry is allowed to flow in the usual way over starch tables, approximately 60% of the starch is deposited. Starch recovery on the tables can be increased by reducing the rate of flow, but only at the expense of lowered quality of the product and reduced plant capacity. When the crude starch is recovered on the solid bowl centrifuge, the prime quality and sludge fractions are packed tightly together. The "Merco" Centrifugal separator effects a satisfactory continuous separation of the high and low quality wheat starch fractions, but the losses of starch remain high with this equipment.

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Starch that is intended for conversion to syrup should have a protein content below 0.4%. With larger amounts of protein impurities, frothing is troublesome in the evaporator, and the finished syrup darkens on standing and is off-flavored. The starch must also be adequately dewatered; the extra amount of acid required to hydrolyze dilute starch slurries (below 20° Bé.) raises the sodium chloride content of the finished syrup sufficiently to impart a salty taste. Our analyses of commercial wheat syrups, obtained from both U.S. and Canadian plants, demonstrated that neither of these requirements was being met in the U.S. and Canadian wheat syrup enterprises (5); the dark color, high nitrogen and sodium chloride contents, and off-flavor were all shown to be caused by the use of dilute wheat starch slurries that contained objectionable amounts of protein impurities (4).

Several explanations have already been offered for the "squeegee" starch phenomenon, which was at least partially responsible for the above problems in wheat syrup manufacture. Wagner (cf. (7)) and MacMasters and Hilbert (14) attributed its formation to small and broken starch granules. MacMasters and Hilbert (14) also suggested polarity of the starch granules, resulting from adsorbed salts, as a possible cause. Sandstedt, Jolitz, and Blish (15) concluded that the "squeegee" starch fraction was caused by partially degraded starch or "amylodextrin". Stern (21) indicated that fiber particles predominated in this fraction. Goldbeck (7, 8) attributed sludge formation to bran particles, and to protein-starch agglomerates. Baker, Parker, and Mize (2) reported that all wheat starch granules possess a thin film of adsorbed pentosan. They concluded that this film was responsible for the "squeegee" starch characteristics; small starch granules usually predominate in this fraction, and they reasoned that the adsorbed pentosan film would have greatest effect on the properties of the small granules, because of their greater surface area per unit of solids.

The interpretation of the "squeegee" starch phenomenon now offered differs from all of the foregoing explanations. The present paper describes the observations on which this new interpretation is based. A practical method is also described for reducing the protein and pentosan contents of crude wheat starch, obtained by the screening process (18), to the level required for the production of first quality syrup.

Experimental

Composition and Properties of "Squeegee" Starch

Crude wheat starch usually settles out by gravity as shown in Fig. 1. When the crude suspension is subjected only to the force of gravity, the starch is distributed about equally between the lower "prime quality" fraction and the discolored and decidedly more voluminous sludge or "squeegee" fraction. The distribution of the starch between these two fractions is not changed by rendering the solution acid or alkaline, but dilute alkali (ammonia or sodium hydroxide) deepens the color of the sludge and increases its volume. On centrifuging the impure sludge in bottles, much of the starch is thrown clear, to form

PLATE I



FIG. 1. Appearance of crude wheat starch after settling by gravity in 0.25 N ammonium hydroxide.

FIG. 2. Appearance of crude wheat starch (left) and of prime quality wheat starch (right), as collected on perforate bowl centrifuge.

FIG. 3. Photomicrograph of pentosan matrix containing embedded starch granules.

a hard bottom cake. The resulting separation of the slimy and hard starch fraction is not clear-cut—considerable starch must always be sacrificed to ensure complete removal of the "squeegee" fraction.

Fig. 2 illustrates the nature of the starch deposits that are obtained when crude and prime quality wheat starch suspensions are collected on the perforate bowl centrifuge. The resuspended prime quality fraction forms a solid white cake on the cloth, similar to that obtained with ordinary corn or potato starch. When crude wheat starch suspension is fed to the perforate bowl centrifuge, a slimy layer of impure starch is deposited. The thin layer shown on the left side of Fig. 2 was impervious to water at 3000 g. and represents the maximum amount of crude wheat starch that could be collected on this type of centrifuge. Water continued to filter through the vastly thicker cake of prime quality wheat starch, shown on the right, under the same centrifugal force.

Voluminous "squeegee" fractions obtained by gravity settling, as illustrated in Fig. 1, were resuspended in water without disturbing the bottom cake, and then centrifuged in bottles. The upper sludge fraction was removed with a spatula, dried in an air tunnel, pulverized, and analyzed for impurities (Table I). The methods of analysis were the same as in an earlier investigation (3).

TABLE I
IMPURITIES IN CEREAL STARCH SLUDGE FRACTIONS, % DRY BASIS

Type of cereal	Pentosan	Protein	Fat	Fiber	Ash
Wheat, Ontario Winter	12.0	Trace	—	3.2	—
Wheat, Blanca var.	5.1	1.5	0.7	3.7	0.5
Wheat, Kharkov var.	8.4	1.6	0.7	3.3	0.8
Wheat, Jones Fife var.	3.7	1.6	0.6	3.5	—
Wheat, Dicklow var.	5.0	3.2	0.8	3.8	0.6
Waxy barley	5.8	1.1	0.7	3.5	5.1
Grain sorghum	4.0	4.0	1.7	3.8	0.9

The fat content of the wheat and barley starch sludges was the same as in prime quality starches (3). The fiber content ranged between 3 and 4%, and was consistently lower than the pentosan content—the pentosan content of the "squeegee" fraction is thus too high to be explained on the basis of bran particles. The ash content of the wheat and sorghum starch sludges was 0.5–0.9%, which is attributed to salts absorbed from the tap water used in the preliminary separation of the starch and gluten. The high ash content of the waxy barley fraction resulted from its exposure to dilute sodium hydroxide. With one exception, the protein contents exceeded 1%. On a weight basis the order of importance of the impurities was pentosan, fiber, protein, fat, and ash. Among these, only the pentosan and fiber were present in larger amounts than in the flours which served as starting materials.

The "Ontario Winter Wheat" sludge fraction (Table I) was subjected to a succession of centrifuging and washing treatments. The sludge obtained by

gravity settling was subjected to six centrifuging treatments at 3000 g. in which only the uppermost slimy layer was successively recovered. The pentosan content of this sample was much higher than that of the less exhaustively treated "squeegee" starch samples. The fiber content remained about the same, and the protein impurities were almost entirely eliminated. Negative tests for nitrogenous compounds were given with Millon's reaction, the Biuret test, and with Lassaigne's test for organic nitrogen. A positive Lassaigne's test was obtained only after allowing the reaction mixture to stand for two hours. Tollens' phloroglucinol color reaction for pentosans developed as strongly with this sample as with powdered bran. Since the protein impurities had been almost entirely removed without affecting the nature of the "squeegee" fraction, they seemed to be eliminated as possible causes of its formation. The pentosan content on the other hand had been more than doubled by concentrating the "squeegee" fraction by repeated centrifugation.

Microscopic Observations

MacMasters and Hilbert (14) have provided photomicrographs of prime quality and "squeegee" wheat starch fractions obtained with transmitted light. Their photographs show only small and broken starch granules in the "squeegee" fraction. When we examined the two starch fractions microscopically by transmitted light in the usual manner, we were not able to confirm their observation of a clear-cut separation of the large and small starch granules. The prime quality wheat starch always contained small starch granules, and the "squeegee" fraction usually contained large unbroken granules as well as small granules. Although the small granules were much more abundant in the "squeegee" fraction, the frequently observed presence of both types of granules in both fractions seemed to rule out granule size as the cause of the "squeegee" starch phenomenon. Rice starch, after all, is composed entirely of microgranules, and yet it does not resemble "squeegee" wheat starch.

Examination of uncovered drops of the suspended "squeegee" starch fraction with a low power binocular microscope by reflected light against a black background revealed the true nature of the "squeegee" fraction. After adding a trace of iodine-potassium iodide solution, the starch grains could be seen embedded in voluminous masses of transparent jelly. The transparency and large size of the jelly masses makes them almost invisible in transmitted light (Fig. 3). Upon tilting the microscope slide, masses containing dozens of starch grains of different sizes were seen to move as individual units. The aggregates were observed to coalesce upon contact to form larger structures. They could be ruptured and the embedded starch granules (damaged and undamaged, large and small) could be teased out. Free starch grains and fiber particles were observed to stick to the outer surface of the jelly masses and remain attached during subsequent movement of the aggregates.

Stereoscopic examination of "squeegee" starch fractions obtained from different varieties of wheat, different grades of flour, as well as from cereals other than wheat (rye, barley, and sorghum) revealed similar jelly aggregates, con-

taining embedded starch granules, as the outstanding feature in all cases. The jelly masses are contaminated with soluble starch except when washed exhaustively on the centrifuge. The amyloextrin staining reaction observed by Sandstedt *et al.* (15) is therefore attributed to an incidental contaminant. The strongly hydrated condition of the jelly complex was evident from the speed with which the deeply embedded starch granules were stained at iodine concentrations that were insufficient to impart a yellow color to the gelatinous mass itself.

Reproduction of the "Squeegee" Starch Phenomenon with Separated Wheat Fractions

The only possible sources of the pentosan jelly responsible for "squeegee" starch formation are the endosperm pentosans, and the "hemicelluloses" of the bran particles. Using Swanson's calculations (22, p. 150) the amount of bran powder in patent, straight, and clear grades of flour is *ca.* 0.4%, 0.8%, and 2.2% respectively.

Wheat bran was Wiley-milled and ball-milled to pass 100 mesh. The final sedimentation volume of this very fine bran powder in water proved to be exceptionally high, 1 gm. occupying 5 ml. after 24 hr. at room temperature. Water suspensions of pure wheat starch and bran powder settled out together as a uniform mixture. The sedimentation volume of the mixture of starch and bran powder equalled but did not exceed the sedimentation volumes of the starch and bran fractions observed separately. Addition of alkali to these mixtures resulted in the marked deepening of color that is a consistent characteristic of the "squeegee" starch fraction. These tests indicated that the bran particles in the original flour would be recovered mainly in the "squeegee" fraction, that they contribute to its bulk, and are at least partially responsible for the deepening of color that occurs on adding alkali.

Table II reports the sedimentation volumes of prime quality wheat starch in distilled water and in water extracts of bran "fines" and of patent flour. The

TABLE II
SEDIMENTATION VOLUMES OF PURE WHEAT STARCH IN WATER AND IN
EXTRACTS OF WHEAT FLOUR AND 100 MESH WHEAT BRAN AT 8°C.

Suspension	Time at 8°C.	
	12 hours	2 weeks
	Sedimentation volume, ml.	
5 gm. starch in 54 ml. water (control)	7.0	7.0
5 gm. starch in 54 ml. bran extract*	13	11
5 gm. starch in 54 ml. flour extract**	19.0	15.5
54 ml. flour extract alone	17.0 (light sludge)	11.0 (light sludge)

* One part bran powder mixed with two parts water for five minutes in a Waring Blendor, and then centrifuged.

** Flour extract was prepared according to Baker, Parker, and Mize (2).

sedimentation volumes were greatly increased by both extracts, the flour extract having the greater effect. On allowing the concentrated flour extract to stand in the absence of added starch, a voluminous sludge formed that could be seen with the unaided eye. The starch that settled out last in the presence of these two extracts was then examined stereoscopically. Although the pure starch by itself showed complete freedom from jelly masses, typical jelly aggregates containing embedded starch granules were found in the "artificial" sludge fractions produced with both bran and flour extracts. The "squeegee" starch complex apparently had been built up from "prime quality" or independent starch granules and water-soluble gums of both the bran and endosperm.

Control Measures

Experiments were done to find methods of reducing the protein content of the crude starch en masse below 0.4% without discarding any of the starch. Schoch (16) had observed that amylose crystallizes out of dilute starch solutions saturated with monohydroxy alcohols such as *n*-butanol or amyl alcohol. The effects of higher alcohols on the "squeegee" pentosan complex were therefore determined. Since the protein impurities were mainly in the "squeegee" fraction, attempts were also made to decompose the jelly aggregates with dilute acid and alkali as well as by autofermentation.

For the experiment reported in Table III, 3500 ml. of crude starch suspension was prepared by the screening process (18). Samples 2, 9-18 (100 ml. each), were transferred directly to stoppered, graduated cylinders, the indicated organic compounds were introduced with vigorous shaking, and the starch was

TABLE III
SEDIMENTATION VOLUMES OF CRUDE WHEAT STARCH IN VARIOUS LIQUIDS
(100 ml. aliquots of crude starch suspension, prepared
by the screening process (18))

Medium	Sedimentation volume at 25°C., ml.	
	After 12 hours	After 24 hours
1. Distilled water	33.0	32.0
2. Tap water	33.0	31.5
3. Tap water, 2 washes	32.0	31.5
4. Tap water, following 2 washes with 0.02 <i>N</i> HCl	33.5	31.5
5. Tap water, following 2 washes with 0.01 <i>N</i> NaOH	42.5	42.5
6. Absolute ethanol	31.0	31.0
7. 75% ethanol	38.5	38.0
8. 50% ethanol	34.3	32.0
9. 25% ethanol	31.0	30.0
10. 30% propanol	37.0	34.0
11. 15% propanol	33.0	32.0
12. Water sat'd with butanol	59.5	55.0
13. Water sat'd with pentanol	48.3	44.0
14. Water sat'd with <i>n</i> -amyl alcohol	46.5	43.0
15. Water sat'd with octanol	38.8	36.0
16. Water sat'd with hexanol	44.0	40.5
17. Water sat'd with lauryl alcohol	39.2	37.0
18. Water sat'd with oleic acid	41.0	38.5

then allowed to settle for 24 hr. Samples 1, 3-8, were centrifuged down completely, and after receiving the indicated treatments were also transferred as uniform suspensions to stoppered cylinders. Each of these samples contained 14 gm. of starch. The sedimentation volume for 14 gm. of prime quality wheat starch in distilled water was 22.0 ml.

None of the 18 treatments applied to the crude starch suspensions reduced the sedimentation volume below 30 ml. Many of the treatments increased the sedimentation volume, e.g., preliminary extraction with dilute alkali or exposure to saturated solutions of the higher alcohols and oleic acid. The pentosan complex assumed a visibly fibrillar structure in the presence of ethanol, but the "brush-heap" structure remained as bulky as in water. Judging from the sedimentation volumes, none of these treatments appeared promising as control measures. The discolored and blotchy appearance shown in Fig. 1 was retained in all cases.

The large difference in sedimentation volume observed after brief exposure to dilute acid (0.02*N* hydrochloric acid) and alkali (0.01*N* sodium hydroxide) prompted an experiment on the effect of pH on crude wheat starch sedimentation volumes. Two-liter aliquots of crude starch suspension were used at each pH level:

pH	2.0	3.0	4.0	5.0	7.0	10.5
Sedimentation volume, ml.	730	810	800	790	800	960

It is apparent that the sedimentation volume is much lower in strongly acid than in strongly alkaline medium. However, only at a pH of 2.0 or less is the sediment significantly less voluminous than at neutrality.

Table IV shows the changes in protein and pentosan content of crude wheat starch resulting from a number of acid digestion treatments. Two liters or more of the crude starch slurry was employed in each treatment. The slurries were continually agitated during the 48 hr. exposure to dilute acids. In the double extraction with hydrochloric acid, the starch was recovered on the bowl centrifuge after 24 hr. and resuspended in fresh dilute hydrochloric acid. Among

TABLE IV

RESIDUAL PROTEIN AND PENTOSAN CONTENT OF CRUDE WHEAT STARCH AFTER 48-HR. EXTRACTION TREATMENTS WITH DILUTE HYDROCHLORIC AND SULPHUROUS ACID SOLUTIONS AT 25°C.

Treatment (16 hours)	Protein content, % d.b.	Pentosan content, % d.b.
Control	0.76	1.34
Single extraction with HCl, pH 2.0, 8° Bé. slurry	0.50	1.18
Single extraction with HCl, pH 1.7, 8° Bé. slurry	0.49	1.32
Double extraction with HCl, pH 2.0, 8° Bé. slurry	0.41	0.68
Single extraction with 0.50% SO ₂ , 8° Bé. slurry	0.49	0.84
Single extraction with 0.35% SO ₂ , 8° Bé. slurry	0.475	1.33
Single extraction with 0.25% SO ₂ , 1.5° Bé. slurry	0.46	0.85

the three 48-hr. hydrochloric acid treatments, the double extraction at pH 2.0 effected the largest reduction in pentosan and protein content. It was also apparent that a similar reduction in content of impurities could be effected with 0.50% sulphur dioxide.

Temperatures of 25°, 35°, 40°, and 45°C. were maintained in the next experiment for 16 hr. during which the 4-liter lots of slurry were continuously agitated (Table V). The residual pentosan content decreased in a regular manner

TABLE V

RESIDUAL PROTEIN AND PENTOSAN CONTENTS OF CRUDE WHEAT STARCH AFTER 16-HR. EXTRACTION TREATMENTS WITH DILUTE HYDROCHLORIC AND SULPHUROUS ACID SOLUTIONS AT VARIOUS TEMPERATURES

Treatment (16 hours)	Protein content, % d.b.	Pentosan content, % d.b.
Control	0.76	1.34
Single extraction with HCl, pH 1.7, 25°C.	0.50	1.32
Double extraction with HCl, pH 1.7, 25°C.	0.48	1.18
Single extraction with HCl, pH 1.7, 35°C.	0.50	1.15
Single extraction with HCl, pH 1.7, 40°C.	0.50	0.85
Single extraction with HCl, pH 1.7, 45°C.	0.44	0.43
Single extraction with 0.5% SO ₂ , 25°C.	0.49	0.84

with increasing extraction temperature. The lowest protein content was obtained at the highest extraction temperature, but the residual protein contents were all *ca.* 0.5% at 25–40°C. None of these treatments caused a significant loss in starch solids.

Table VI reports an experiment in which the extraction temperature was maintained at 45°C. with pH values of 1.7, 2.0, and 3.0, the time of extraction being varied from 4 to 32 hr. At pH 3.0, the pentosan content was not reduced. At pH 2.0 and 1.7, the pentosan content was reduced to less than one-third of the original value. The protein content remained above 0.5% after 32 hr.

TABLE VI

RESIDUAL PROTEIN, PENTOSAN, AND SOLIDS RECOVERED BY CENTRIFUGING, AFTER EXTRACTING CRUDE WHEAT STARCH SLURRIES IN DILUTE HYDROCHLORIC ACID AT 45°C.

Extraction time, hr.	Protein content of recovered starch, % d.b.			Pentosan content of recovered starch, % d.b.			Solids recovered on solid bowl centri- fuge, %		
	pH 1.7	pH 2.0	pH 3.0	pH 1.7	pH 2.0	pH 3.0	pH 1.7	pH 2.0	pH 3.0
0	0.74	0.74	0.74	1.48	1.48	1.48	100	100	100
4	0.34	0.59	0.53	1.24	1.28	1.46	99	99	100
8	0.37	0.41	0.55	1.16	0.99	1.35	99	99	100
16	0.44	0.35	0.55	0.91	0.69	1.43	99	99	100
32	0.38	0.38	0.56	0.30	0.41	1.38	98	97	98.5

extraction at pH 3.0. At pH 2.0 and 1.7, the protein content was consistently reduced to *ca.* 0.4% by eight-hour and longer extraction periods. Beyond removing impurities these treatments did not reduce the yield of dry starch by more than 1%. Although the paste viscosity is greatly reduced by these treatments, this change should not reduce usefulness for conversion to syrup.

The pentosans and proteins were not removed from the "squeegee" starch by autofermentation. Their degradation and removal by micro-organisms of high "pentosanase" activity is an interesting possibility that has not as yet been investigated.

Discussion

Goldbeck many years ago (7) stressed the need for a better understanding of wheat starch sludge or the "squeegee" fraction since it would be possible to introduce control measures only when the cause of this phenomenon had been clarified. The observations presented in this paper have established that the "squeegee" fraction is caused by hydrophilic pentosans derived from the endosperm and bran. This fraction is not caused by broken or small starch granules, although the smaller granules do predominate in it. Their presence in greater numbers in the jelly masses results from their lower sedimentation velocity in a viscous medium: the largest starch granules are thrown clear under a sufficiently high centrifugal force. Baker *et al.* (2), indicated that all wheat starch granules possess a film of adsorbed pentosan, and that the properties of small starch granules were affected to a greater extent by this film because of their greater surface area per unit of solids. Baker's explanation has been previously shown by us to be incorrect on analytical grounds (3); there has also been no evidence of pentosan films on individual granules of the prime quality fraction when examined by reflected light under the binocular microscope.

The fact that the pentosan of the "squeegee" fraction was not precipitated by the higher alcohols suggests that this polysaccharide has a branched structure; gel formation is a characteristic of branched rather than of linear polymers.

Although the protein content of typical "squeegee" fractions is normally much higher than that of the hard or prime quality starch, the protein impurities should be regarded as incidental occlusions in the heterogeneous jelly masses rather than as causal agents. In past industrial applications of the screening process, the protein content of the crude starch *en masse* was usually *ca.* 1.5% instead of 0.75% as was observed consistently in the present studies. The greater contamination with protein that occurred consistently in industrial operations arose at the batter disintegration stage. Shewfelt and Adams (18) prescribe three minutes vigorous agitation of the slack dough in an excess of water to obtain the desired curdlike suspension of gluten. This agitation treatment must be carefully controlled. If disintegration of the gluten proceeds too far, as was normally the case in industrial applications, much of the gluten passes the gyratory screen and is collected in the "squeegee" fraction.

A possible method of raising the purity of crude wheat starch to the level required for producing first quality syrup consists of digesting the starch suspensions at pH 2.0 for approximately one day at *ca.* 45°C. before recovering the starch on the solid bowl centrifuge. This treatment reduces the protein content below 0.5% without any reduction in the starch yield. An ideal control method, which remains to be developed, would consist in digesting the crude starch suspensions with selective enzymes that would remove the impurities while leaving the starch granules intact.

The manufacture of wheat starch and syrup has a much longer history than the corn starch industry. The supplanting of wheat by corn as a source of cereal starch is usually attributed to the difference in price and starch content of the two types of grain. The "squeegee" wheat starch fraction was likely a contributing factor as well. These pentosan complexes are equally troublesome in the manufacture of starch from rye and barley. Besides its high content of starch and oil, corn offers the further advantage as a starch source over other cereal grains of having a low content of hydrophilic pentosans.

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CANADIAN ERUCIC ACID OILS

V. PHYSICAL, CHEMICAL, AND EDIBLE PROPERTIES OF OIL FROM WEED SEED SCREENINGS¹

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Abstract

Monthly samples of cleaned weed seed screenings and of screenings oil (commercially solvent extracted) examined over a six-month period indicated that the composition of the screenings varied widely but that of the oil was remarkably constant. The composition of the weed seed was: wild mustard, mostly *Brassica arvensis* (53-79%, av. 68%), mixed weed seeds (13-35%, av. 23%), crop seeds (4-10%, av. 6.6%), and broken and unidentified seeds (1-6%, av. 3%). The average characteristics of the oil were: iodine value, 124; saponification number, 182; free fatty acid (as oleic), 2%; relative light transmission (cf. mineral oil), 5% at 440 m μ , 18% at 540 m μ , 26% at 660 m μ . Appearance of the oil and response to processing were similar to those of rape and mustard seed oils. Small scale taste panel tests indicated that processed screenings oil was generally not as palatable as corn or cottonseed salad oils, but that screenings shortening was generally as acceptable as the control (commercial vegetable shortenings). The screenings shortening had a satisfactory smoke point and good baking volume properties.

Introduction

Rapeseed, mustard seed, and stinkweed seed oils may be used as edible fat sources as well as for industrial purposes (3, 7-10). During 1948 a plant using the solvent extraction process for removal of oil from weed seed screenings commenced operations at Fort William. The screenings contain large amounts of wild mustard and the oil might be expected to be similar to other erucic acid oils. This paper describes the composition of weed seed screenings, and the chemical and physical properties of the oil, its response to processing, and its edible properties.

Materials and Methods

Source Material

In the Fort William plant, accumulated screenings from cereal crops of the prairies are passed through cleaners to remove gross impurities such as dust, chaff, and straw. Samples were taken directly from the stream from the cleaners to the preheaters, flakers, and extractors. Collections of seed were made monthly from November 1948 to April 1949 and subjected to botanical analysis. Seed samples of 25 gm. were analyzed by the Plant Products Division, Science Service, Dominion Department of Agriculture, Ottawa. In addition, the *Brassica* seeds in 2-gm. subsamples were examined to determine if they were all wild mustard species (*Brassica arvensis*, *B. juncea*, *B. nigra*, and *B. campestris*).

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The results, Tables IA and IB, show that the content of wild mustards ranged from 53% to 79%, with an average of 68%. Crop seeds comprised alfalfa, alsike, barley, millet, oats, red clover, rye, sweet clover, timothy, and wheat, and varied from 4% to 10%; flax was present in measurable quantities in only two of the samples, the maximum amount being 0.75%. Mixed weed seeds content varied from 13% to 35%, with an average for the six samples of 22.6%. Inert matter comprised many small pieces of broken wild mustard and other seeds which could not be identified; the amounts ranged between 1 and 6%.

TABLE IA

ANALYSIS OF SIX COLLECTIONS OF WEED SEED SCREENINGS BY PLANT PRODUCTS DIVISION,
SCIENCE SERVICE, DOMINION DEPARTMENT OF AGRICULTURE, OTTAWA
(Per cent by weight)

Seed	Monthly seed collections, 1948-1949						
	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	Average
Pure seed, <i>Brassica</i> spp.* (appear to be all wild mustard)	69.05	52.68	73.61	59.20	72.17	79.05	67.63
Mixed weed seeds**	22.32	34.52	17.12	27.84	21.21	12.64	22.61
Crop seeds	4.20 ^a	6.38 ^b	7.63	10.04	5.70	5.68	6.61
Inert matter***	4.43	6.42	1.64	2.92	0.92	2.63	3.16

* Predominantly *Brassica arvensis* ("charlock") but considerable numbers of *B. juncea* present. A trace of *B. alba* was found in samples Dec. and Feb. It is very probable that *B. nigra* and *B. campestris* may also be present in limited numbers.

^a Contains 0.39% flax seed, based on original sample weight.

^b Contains 0.76% flax seed, based on original sample weight.

** Detailed analysis of mixed weed seeds in Table IB.

*** Inert matter includes many small pieces of broken wild mustard and other seeds which could not be identified.

The 38 different kinds of weed seeds present are enumerated in Table IB. Most of the weed seeds occurred in traces to small amounts. However, lamb's-quarters were present in relatively large amounts, the average for all six collections being about 9%, with a low occurrence of 3% and a high of nearly 16%. The content of Russian thistle varied between 0.5% and 10%. Green foxtail, hare's-ear mustard, wild buckwheat, and stinkweed were present in relative abundance.

Extraction

Cleaned screenings are subjected commercially to a heat treatment and then flaked and passed to extractors where oil is removed by a warm paraffinic solvent. The solvent is removed from the oil by distillation and steam stripping. Alkali in carefully controlled amounts is stirred into the solvent-free oil prior to transfer of the oil to a settling tank (this treatment does not constitute alkali refining but promotes settling of impurities). Oil is allowed to stand in the settling tank (11,000 Imp. gal.) for a minimum period of 48 hr. when the best quality top oil is transferred to final storage vessels (each 12,500 Imp. gal.).

TABLE IB

DETAILED ANALYSIS OF MIXED WEED SEEDS BY PLANT PRODUCTS DIVISION,
SCIENCE SERVICE, DOMINION DEPARTMENT OF AGRICULTURE, OTTAWA
(Per cent by weight)

Seed	Monthly seed collections, 1948-1949					
	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.
American dragonhead	<0.24	—	<0.46	<0.66	<0.44	<0.17
Ball mustard	<0.39	0.59	—	<0.62	<0.55	0.12
Barnyard grass	<0.24	<0.29	<0.46	<0.66	<0.44	<0.17
Bladder Campion	—	—	<0.54	—	<0.55	—
Canada thistle	<0.39	0.26	<0.54	<0.62	<0.55	<0.10
Catch fly	—	—	<0.54	0.21	<0.55	<0.10
Chicory	—	—	—	<0.62	—	—
Cinquefoil	<0.24	<0.29	<0.46	—	—	—
Common plantain	<0.24	—	—	—	—	—
Couch grass	—	—	—	—	<0.55	—
Cow cockle	0.58	—	0.49	<0.62	—	—
Dock	<0.39	<0.29	<0.54	<0.62	<0.55	<0.10
Dodder	—	<0.29	—	—	—	<0.10
Dog mustard	<0.63	1.71	<0.54	0.31	0.11	<0.06
False flax	<0.39	—	—	<0.62	—	<0.06
False ragweed	<0.39	—	—	—	—	—
Green foxtail	0.35	5.72	1.53	1.48	1.33	1.16
Hare's-ear mustard	1.34	1.27	2.02	5.69	4.58	3.55
Hemp nettle	<0.24	—	—	—	<0.44	<0.17
Knotweed	—	—	—	<0.66	<0.44	—
Lady's thumb	<0.24	0.45	0.54	<0.66	<0.44	<0.17
Lamb's-quarters	7.05	15.87	7.78	11.55	8.29	3.15
Night flowering catchfly	<0.39	0.27	—	—	—	—
Old witch grass	<0.24	<0.29	<0.46	—	—	—
Perennial sow thistle	—	<0.29	<0.54	<0.62	<0.55	—
Pigweed	—	—	—	—	<0.44	—
Plantain	—	<0.29	<0.46	—	—	—
<i>Polygonum</i> spp.	—	—	1.43	—	—	—
Poverty weed	—	<0.29	<0.46	—	—	—
Russian pigweed	<0.24	0.33	<0.46	<0.66	<0.44	<0.17
Russian thistle	10.12	3.71	0.56	2.11	3.44	1.49
Stinkweed	0.64	2.09	1.52	1.38	1.15	0.39
Stickseed	<0.39	<0.29	<0.54	<0.62	<0.55	0.07
Stitchwort	—	<0.29	—	—	—	—
Tumbling mustard	<0.63	0.55	<0.46	—	<0.55	<0.06
Western false flax	—	—	<0.54	—	—	—
Wild buckwheat	0.98	1.41	—	3.83	1.32	2.38
Wormseed mustard	<0.24	<0.29	<0.46	—	<0.44	<0.06

< This symbol before a particular percentage indicates that all samples so marked in any one column were together equal to that quantity.

Tests on Oil Samples

Two 25 gal. samples of settled weed screenings oil were obtained in early and late October, 1948, and are designated as lots 5-10-48 and 20-10-48. These samples were used in study of behavior on refining and for preparation of edible products. Subsequently, a one-gallon sample of settled oil was obtained each month from October, 1948, to April, 1949, except in November when two samples were taken—a total of eight samples (Table II).

Crude oils from the 25-gal. lots were subjected to various bleaching and refining treatments followed by determination of free fatty acid content,

and relative light transmission using Stanolax as a standard (Tables III and IV). The monthly collections were compared in the crude condition and after a simple bleaching procedure, determinations being made of free acidity, iodine value, saponification number, and relative transmission by methods previously described (2).

Spectrophotometric analyses with a model D-U Beckman instrument were made of the oils for content of linoleic, linolenic, and arachidonic acids (1). A crude erucic acid fraction was separated by crystallization from acetone solution at -40°C .

Investigation of Edible Properties

Salad oils and shortenings were prepared in duplicate by standard methods (9, 10) from each of two 25 gal. batches of crude weed seed oil already described. These oils and shortenings were compared *per se* with commercial salad oils (corn and cottonseed) and vegetable shortenings, and also as materials in the preparation of mayonnaise, pastry, and doughnuts. All comparisons were made using both fresh and aged (10 days at 100°F .) oils and shortenings. The oils and mayonnaises were appraised for color, texture, odor, and flavor; and the pastry and doughnuts for odor and flavor. Test samples were scored in random groups of four by a 24-member panel. Appraisals were scored in the usual way (4-6) by assigning the integers from -5 through zero to +5 to 11 gradations of subjective reaction ranging from "gross deficiency" through "preferred level" to "gross excess" of each characteristic considered.

Measurements of melting point, iodine value, light transmission, fluorescence, viscosity, peroxide oxygen, free fatty acid, and smoke point were made on all oils and shortenings (10). Baking volume tests were made with the screenings shortening and with the mustard and stinkweed shortenings prepared in earlier studies (7, 10). These shortenings were "plasticized" according to a laboratory procedure (10).

Results

Physical and Chemical Properties

Solvent extracted oil from weed seed screenings is similar in appearance to expressed rapeseed and mustard seed oils. Table II shows free fatty acid content, saponification number, iodine value, and relative transmission for the monthly collections of crude oils before and after a simple bleaching treatment. Free fatty acid content of crude oils varied from 0.9% to 2.3%. Saponification numbers and iodine values were generally closely similar for all samples. Relative transmission was only 5% for all oils at the lowest wave length, with rather wide variations being shown at the two higher wave lengths. Notwithstanding the general chemical similarity of the oils, considerable difference in ease of bleaching was demonstrated.

The results of various bleaching treatments of the two oil collections used in the study of edible properties are given in Table III. Various concentrations of Superfiltrol or of A.O.C.S. clays had little effect on the free fatty acid content

TABLE II
CHARACTERISTICS OF CRUDE AND BLEACHED WEED SEED OILS
(One-gallon samples)

Month of collection	Free fatty acid, % as oleic.	Saponification number, mgm. KOH per gm.	Iodine value, cgm. per gm.	Relative transmission, % at:		
				440 mμ	540 mμ	660 mμ
Crude oils						
October	2.0	179.2	124.8	5	21	30
Early Nov.	1.1	185.0	123.5	5	20	26
Late Nov.	0.9	180.1	124.6	5	33	40
December	1.3	183.5	124.9	5	20	25
January	1.5	183.2	123.3	5	19	26
February	2.3	181.4	125.4	5	12	20
March	1.4	179.4	124.4	5	13	21
April	2.5	182.2	122.8	5	11	20
Crude oils after bleaching with 4% Superfiltrol at 100°C. for 20 min.						
October	2.0	182.9	124.0	13	80	93
Early Nov.	1.2	182.2	125.3	17	82	93
Late Nov.	0.9	181.0	126.2	38	93	99
December	1.4	182.9	125.6	49	93	98
January	1.5	183.3	125.8	9	78	95
February	2.3	182.0	123.7	22	79	90
March	1.4	183.3	123.8	27	85	95
April	2.5	181.8	124.4	14	76	89

TABLE III
EFFECT OF CLAY, CONCENTRATION, AND TEMPERATURE, ON BLEACHING OF
CRUDE WEED SEED OILS

Temperature, °C.	Oil from 5-10-48 lot of 25 gal.			Oil from 20-10-48 lot of 25 gal.		
	F.F.A., % as oleic	Relative transmission, % at:		F.F.A., % as oleic	Relative transmission, % at:	
		440 m μ	660 m μ		440 m μ	660 m μ
Crude oil	1.2	5	32	0.8	5	33
Crude oil bleached with 2% Superfiltrol clay for 20 min.						
65°	1.3	19	85	0.7	14	91
100°	1.2	23	94	0.8	11	91
125°	1.4	22	83	0.8	17	89
200°	1.9	22	83	1.2	34	91
Crude oil bleached with 4% Superfiltrol clay for 20 min.						
65°	1.0	13	91	0.7	27	94
100°	1.0	22	92	0.8	36	93
125°	1.0	24	92	0.8	44	92
200°	1.2	23	95	2.2	35	95
Crude oil bleached for 20 min. with 4% A.O.C.S. clays.						
100° (Fuller's earth)	1.4	6	72	0.6	5	78
100° (Activated earth)	1.4	46	94	0.7	33	91

of the oils, with the exception of bleaches made at 200°C. for which marked increases were noted. These crude oils were generally similar in color to crude expressed mustard seed oil (3). A feature of the results was the extent of bleaching achieved by 2% Superfiltrol at 65°C.

The responses of the two 25 gal. samples of crude oil to alkali refining and bleaching are described in Table IV. Alkali refining did not improve relative

TABLE IV
THE EFFECT OF CLAY CONCENTRATION ON THE BLEACHING OF ALKALI REFINED
WEED SEED OIL FROM TWO COLLECTIONS

Clay	Oil from 5-10-48 lot of 25 gal.			Oil from 20-10-48 lot of 25 gal.		
	F.F.A., % as oleic	Relative transmission, % at:		F.F.A., % as oleic	Relative transmission, % at:	
		440 m μ	660 m μ		440 m μ	660 m μ
0% Superfiltrol	0.01	5	50	0.05	5	56
1% Superfiltrol	0.01	6	77	0.04	29	89
2% Superfiltrol	0.01	30	98	0.08	50	97
4% Superfiltrol	0.04	57	96	0.11	67	95
6% Superfiltrol	0.04	70	102	0.14	75	97
4% A.O.C.S. Fuller's earth	0.17	13	87	0.10	21	89
4% A.O.C.S. Activated earth	0.10	71	96	0.18	71	93

transmission at 440 m μ . Increasing Superfiltrol concentration raised transmission greatly, particularly at the lower wave length. The oil of 20-10-48 showed the greater ease of bleaching, results with 1% Superfiltrol being particularly striking. The A.O.C.S. activated earth was about equally effective with both oils, and was a little more effective than the same concentration of Superfiltrol.

The results of spectrophotometric analyses of variously refined and crude weed seed oils for content of diene, triene, and tetraene acids are given in Table V and reported as linoleic, linolenic, and arachidonic acids. It is apparent from Part A of the table that refining treatments had comparatively little effect on the fatty acid contents. Consequently, the monthly collections of crude oil were subjected to analysis without refining treatment, the data appearing in Part B of the table. A mere trace of tetraene acid was suggested by the results, linolenic acid varied from 12.2% to 14.8%, linoleic varied from 22.5% to 25.3%. The acetone-insoluble acid fraction (crude erucic acid) obtained on crystallization of the fatty acids at -40°C. varied from 11% to 26%.

Properties of Preparations for Edible Use

The melting points and iodine values of the experimental and commercial oils and shortenings were generally similar, as shown in Table VI. Tables VII

TABLE V
 SPECTROPHOTOMETRIC ANALYSES OF WEED SEED OILS

Description	Acid, %		
	Linoleic	Linolenic	Arachidonic
A. Effects of refining treatment on apparent concentrations of diene, triene, and tetraene acids			
Crude from 25 gal. lot of 5-10-48:	22.1	15.8	0.2
Bleached with 4% Superfiltrol at 65°C.	20.3	16.0	0.1
Bleached with 4% Superfiltrol at 200°C.	20.0	13.0	0.4
Alkali refined	21.1	12.9	0.1
Alkali refined, bleached with 4% Superfiltrol at 100°C.	21.7	15.0	0.1
Alkali refined, bleached with 6% Superfiltrol at 100°C.	20.6	14.4	0.0
Crude from 25 gal. lot of 20-10-48:	22.6	14.7	0.3
Alkali refined, bleached with 4% Superfiltrol at 100°C.	20.8	14.8	0.0
Alkali refined, bleached with 6% Superfiltrol at 100°C.	22.7	15.3	0.0
B. Polyunsaturated acid composition of a series of samples			
Crude oil, month of collection:			
October	23.6	13.7	0.1
Early November	24.3	14.3	0.1
Late November	22.5	14.8	0.1
December	25.3	13.1	0.1
January	25.0	13.6	0.1
February	24.8	12.2	0.2
March	25.3	12.3	0.1
April	24.5	13.0	0.2

and VIII present average values for chemical and physical characteristics of the oils and shortenings at various stages of processing and use.

Processed screenings oil showed greater transmission at 440 $m\mu$ than commercial oil, and about the same transmission at 660 $m\mu$ (Table VII). Fluorescence in ultraviolet light (375 $m\mu$) and viscosity were both higher for the

 TABLE VI
 MELTING POINT AND IODINE VALUE OF TEST SAMPLES

Material	Melting point, °C.	Iodine value
Corn oil	—	124.7
Cottonseed oil	—	110.7
Commercial shortening No. 1	41.8	58.0
Commercial shortening No. 2	43.1	66.4
Screenings oil 5-10-48	—	125.4
Screenings shortening, Trial 1	44.2	60.7
Screenings shortening, Trial 2	44.4	61.1
Screenings oil 20-10-48	—	123.5
Screenings shortening, Trial 1	43.6	65.2
Screenings shortening, Trial 2	47.4	62.6

TABLE VII
AVERAGE VALUES FOR CHEMICAL AND PHYSICAL CHARACTERISTICS OF OILS AT VARIOUS STAGES OF PROCESSING AND USE

Characteristic	Test oil	Condition of test material*						
		Crude	Alkali refined	Bleached	Deodorized (fresh)	Aged	Fresh, fried	Aged, fried
Light transmission, % at 440 m μ , relative to mineral oil	Commercial Screenings	— 5	— 5	— 50	44 64	45 60	40 51	40 43
Light transmission, % at 660 m μ , relative to mineral oil	Commercial Screenings	— 33	— 52	— 99	98 99	98 98	96 98	97 99
Fluorescence, Coleman photofluorometer units, 1 gm. of oil in 100 ml. xylol, corrected for fluorescence of xylol	Commercial Screenings	— 76	— 15	— 63	33 72	35 74	35 82	36 72
Viscosity, centistokes at 130°F.	Commercial Screenings	— 21.6	— 21.6	— 21.8	19.9 22.4	19.9 22.2	20.1 22.5	20.2 22.6
Peroxide oxygen value, ml. of 0.002 N thiosulphate per gm.	Commercial Screenings	— 8.0	— 6.0	— 5.2	3.3 0.0	7.8 6.9	3.7 7.0	1.4 7.0
Free fatty acid, as % oleic	Commercial Screenings	— 1.0	— 0.0	— 0.1	0.1 0.0	0.1 0.2	0.1 0.2	0.1 0.2
Smoke point, °F.	Commercial Screenings	— 345	— 428	— 404	434 410	438 412	438 405	438 404

* The commercial oils were used as purchased, and received no further processing.

screenings oils. Peroxide value, free fatty acid, and smoke point were generally of the same order for both oils.

For the shortenings, the screenings and commercial products had similar transmission values (Table VIII). Transmission values at 660 m μ are not shown, as they were all about 95%. Fluorescence and viscosity were both higher for screenings shortening than for commercial shortening. Peroxide value, free fatty acid, and smoke point were similar for both types of shortenings.

TABLE VIII
AVERAGE VALUES FOR CHEMICAL AND PHYSICAL CHARACTERISTICS OF SHORTENINGS AT VARIOUS STAGES OF PROCESSING AND USE

Characteristic	Test shortening	Condition of test material*					
		Undeodorized	Deodorized (fresh)	Aged	Fresh, fried	Aged, fried	
Light transmission, % at 440 m μ , relative to mineral oil	Commercial Screenings	— 52	67 64	65 63	45 39	49 44	
Fluorescence, Coleman photofluorometer units, 1 gm. of oil in 100 ml. xylol, corrected for fluorescence of xylol	Commercial Screenings	— 50	14 52	13 38	22 40	20 41	
Viscosity, centistokes at 130°F.	Commercial Screenings	— 30.1	26.9 30.4	27.0 30.3	26.9 30.4	27.0 30.3	
Peroxide oxygen value, ml. of 0.002N thiosulphate per gm.	Commercial Screenings	— 0.0	0.0 0.0	0.0 0.0	1.9 1.4	2.1 2.5	
Free fatty acid, as % oleic	Commercial Screenings	— 0.0	0.1 0.0	0.1 0.2	0.1 0.3	0.1 0.3	
Smoke point, °F.	Commercial Screenings	— 408	405 404	393 399	400 395	395 401	

* The commercial shortenings were used as purchased, and received no further processing.

For both oils and shortenings (Tables VII and VIII), light transmission at 440 m μ decreased with use for deep fat frying of doughnuts, but transmission at 660 m μ was unchanged. Changes in fluorescence were somewhat erratic. Viscosity, peroxide value, and free fatty acid content increased slightly with processing or use of the fats, while smoke point (except for the crude screenings oil) showed a slight decrease.

Baking volume tests showed that screenings, mustard, and stinkweed shortenings gave volumes that were not significantly different from baking volumes obtained with the two commercial vegetable shortenings.

The chemical and physical measurements indicated that the screenings oils and shortenings did not differ from the commercial oils and shortenings to any important extent that might influence food use.

Taste Panel Tests

Average taste panel scores for the oils alone are summarized in Table IX. When fresh, the reference sample of corn oil was rated as definitely too dark in color and the processed weed oils from the second trials of both batches of crude oil as slightly too light. After aging, the corn oil was rated as slightly lighter and the weed oil from one trial processing as slightly darker, but objection to the color of all samples was still in evidence. Appraisals of texture, odor, and flavor were not significantly affected by aging, so Table IX accordingly lists the average scores for these characteristics of both the fresh and aged samples of each type. The only significant feature of the texture appraisals was that the corn oil was rated as slightly too thick, whereas all four weed oil samples were of the preferred consistency (although actually higher in viscosity). The corn oil was considered too strong in both odor and flavor while, of the weed oil preparations, one was rated as slightly deficient in the desired odor and two others were considered to have rather too strong a flavor.

TABLE IX
AVERAGE SUBJECTIVE APPRAISAL SCORES FOR VEGETABLE OILS

Test material	Color		Texture (av. fresh and aged)	Odor (av. fresh and aged)	Flavor (av. fresh and aged)
	Fresh	Aged			
Corn oil	+1.8	+1.3	+0.3	+1.5	+2.1
Cottonseed oil	+0.1	-0.3	-0.1	-0.2	0.0
Screenings oil:					
5-10-48, Trial 1	-0.1	0.0	0.0	+0.1	+0.4
Trial 2	-0.4	-0.4	0.0	-0.2	+0.2
20-10-48, Trial 1	0.0	+0.3	0.0	0.0	+0.6
Trial 2	-0.9	-0.4	0.0	-0.3	-0.1
Statistically significant difference (5% level):					
Between any two averages	0.5	0.5	0.3	0.4	0.4
Of any one average from zero	0.4	0.4	0.3	0.3	0.3

Mayonnaises made from each of the four weed oils, both fresh and aged, were rated as satisfactory in respect to color, texture, and odor, but as having a very slight excess flavor, the average score for all four weed oil samples being +0.3 with a "necessary difference" from zero of 0.3 (Table X). Of the two reference standards, the corn oil (both fresh and aged) produced mayonnaises too strong in odor and flavor, and those from the fresh (but not from the aged) corn oil were slightly too dark in color. Mayonnaise incorporating aged cottonseed oil was thought to be slightly too thick, but in other respects the mayonnaises obtained from this material were rated satisfactory.

TABLE X
AVERAGE SUBJECTIVE APPRAISAL SCORES FOR MAYONNAISES
INCORPORATING TEST OILS

Mayonnaise incorporating:	Color		Texture (av. fresh and aged)	Odor (av. fresh and aged)	Flavor (av. fresh and aged)
	Fresh	Aged			
Corn oil	+0.5	-0.4	0.0	+0.5	+1.4
Cottonseed oil	0.0	-0.2	+0.8	+0.1	+0.2
Screenings oil:					
5-10-48, Trial 1	0.0	0.0	0.0	+0.1	+0.3
Trial 2	0.0	+0.1	0.0	+0.2	+0.2
20-10-48, Trial 1	0.0	0.0	-0.1	+0.1	+0.5
Trial 2	0.0	+0.1	0.0	0.0	+0.2
Statistically significant difference (5% level):					
Between any two averages	0.3	0.4	0.4	0.3	0.4
Of any one average from zero	0.2	0.4	0.4	0.2	0.3

No effect of aging was detected in the appraisals of odor and flavor of pastry cooked with either the test oils or the shortenings prepared from them. Table XI accordingly lists the average scores for both fresh and aged materials. The odor appraisals were satisfactory in all instances. Shortenings from all four weed oils also gave satisfactory flavor results, but use of the oils as such resulted in the recording of a slightly strong flavor.

Scores for odor and flavor of doughnuts cooked in fresh and aged oils and shortenings also are averaged in Table XI, as aging did not significantly affect the relative appraisals. The doughnuts cooked in weed seed oils were rated as having a slightly strong odor but the weed shortenings did not differ significantly from the reference shortenings in this respect. The flavor of the doughnuts cooked in either weed seed oils or shortenings was regarded as generally satisfactory.

The taste panel results indicated that processed screenings oil was generally not as palatable as corn or cottonseed oils, but that screenings shortening was generally as acceptable as the commercial shortenings.

TABLE XI
AVERAGE SUBJECTIVE APPRAISAL SCORES FOR PASTRY AND DOUGHNUTS MADE
WITH TEST OILS AND SHORTENINGS

(Averages for fresh and aged oils and shortenings)

Test material	Pastry		Doughnuts	
	Odor	Flavor	Odor	Flavor
Corn oil	0.0	-0.1	0.0	+0.3
Cottonseed oil	+0.1	0.0	+0.2	0.0
Screenings oil:				
5-10-48, Trial 1	0.0	+0.4	+0.5	+0.1
Trial 2	+0.1	+0.4	+0.5	-0.2
20-10-48, Trial 1	+0.1	+0.4	+0.6	0.0
Trial 2	+0.2	+0.3	+0.4	+0.1
Statistically significant difference (5% level):				
Between any two averages	0.3	0.4	0.3	0.3
Of any one average from zero	0.3	0.3	0.3	0.3
Commercial shortening No. 1	0.0	+0.3	+0.2	0.0
Commercial shortening No. 2	0.0	0.0	+0.2	0.0
Screenings shortening:				
5-10-48, Trial 1	0.0	+0.1	+0.2	+0.1
Trial 2	-0.2	-0.2	+0.2	+0.2
20-10-48, Trial 1	-0.1	0.0	+0.3	+0.1
Trial 2	0.0	-0.1	+0.2	0.0
Statistically significant difference (5% level):				
Between any two averages	0.3	0.3	0.3	0.3
Of any one average from zero	0.3	0.3	0.2	0.2

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